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National Inventory of Natural Sources and Emissions of Sulphur Compounds



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Report EPS 3-AP-79-2

Air Pollution Control Directorate
February 1980

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NATIONAL INVENTORY OF NATURAL SOURCES AND EMISSIONS OF SULPHUR COMPOUNDS

Pollution Data Analysis Division
Air Pollution Programs Branch
Air Pollution Control Directorate

Report EPS 3-AP-79-2
February 1980

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ABSTRACT

Total emissions of sulphur from natural sources in Canada have been estimated at about 500 000 tonnes a year. The emission estimates were obtained through a literature review of sulphur release mechanisms normally associated with biological and other natural processes. The estimates are presented, for the most part, on a census division basis and are likely to be accurate to within an order of magnitude, and therefore should be considered preliminary and subject to revision.

The principal sulphur compound emitted from biogenic sources into the atmosphere is hydrogen sulphide. Others that have been identified include: carbon disulphide, carbonyl sulphide, dimethyl sulphide, dimethyl disulphide and methyl mercaptan. Biogenic sources include soils, water bodies and vegetation.

Other natural sources that have been reviewed in this report are sea spray and lake spray, emitters of sulphate, and forest fires, a minor source of sulphur dioxide emissions. Sulphate is also emitted through wind entrainment of soil dust while hot springs release hydrogen sulphide.

RÉSUMÉ

Au Canada, les émissions totales de soufre d'origine naturelle sont évaluées à environ 500 000 tonnes métriques par année. Les estimés d'émissions ont été développés suite à une revue approfondie de la littérature concernant les mécanismes de dégagements du soufre reliés aux processus biologiques et autres processus naturels. Dans la plupart des cas les estimés sont présentées au niveau des divisions de recensement (comtés) et sont probablement justes à un ordre de grandeur près. Par conséquent, ces estimés devraient être considérées comme préliminaires et sujettes à des changements.

Le principal composé de soufre d'origine biologique, émis dans l'atmosphère, est le sulfure d'hydrogène. Parmi les autres recensés figurent le bisulfure de carbone, le sulfure de carbonyle, le sulfure de diméthyle, le bisulfure de diméthyle et le méthane-thiol. Ces composés proviennent des sols, du milieu aquatique et de la végétation.

Au nombre des autres sources naturelles étudiées dans le présent rapport, notons les embruns formés au-dessus de la mer et des lacs, qui renferment des sulfates, et les incendies de forêt, qui émettent du dioxyde de soufre. Des sulfates s'échappent aussi de la poussière du sol par l'action du vent tandis que les sources thermales émettent du sulfure d'hydrogène.

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GLOSSARY

Unit

Mass:

μg = microgram = 10^{-6} grams
 mg = milligram = 10^{-3} grams
 g = gram

t = metric ton (tonne) = 10^6 grams

Tg = teragram = 10^{12} grams

Area:

ha = hectare = 10^4 square metres
 $= 10^{-2}$ square kilometres

Concentration:

$\mu\text{g S/m}^3$ = micrograms (of a sulphur compound)
 as sulphur per cubic metre

Transfer and Emission Rates:

g S/h = grams (of a sulphur compound) as
 sulphur per hour
 Tg S/yr = teragrams (of a sulphur compound)
 as sulphur per year

Note: all concentrations and emission rates are based on sulphur unless otherwise specified; for example:

$$\begin{aligned} 1 \mu\text{g SO}_2/\text{m}^3 &= 0.5 \mu\text{g S/m}^3 \\ 1 \mu\text{g H}_2\text{S}/\text{m}^3 &= 0.94 \mu\text{g S/m}^3 \end{aligned}$$

Definitions

Flux:

quantity flowing across a given area per unit of time.

Sulphur Budget:

amount of sulphur accounted for in a system over a specified period of time (e.g., Sulphur in-Sulphur out = Original amount of Sulphur in system).

Atmospheric Particulate Loading:

total amount of pollution in particulate form added to the atmosphere in a given period of time.

Chemical Nomenclature

carbonyl sulphide:	COS	methyl mercaptan:	CH_3SH
carbon disulphide:	CS_2	elemental sulphur:	S
dimethyl sulphide:	DMS	sulphur dioxide:	SO_2
dimethyl disulphide:	DMDS	sulphate:	SO_4
hydrogen sulphide:	H_2S		

1 SUMMARY

A principal objective of Environment Canada's Long-Range Transport of Air Pollutants (LRTAP) Program is to develop the capability to assess and predict present and future distributions and depositions of air pollutants in North America. Emission inventories of such pollutants for Canada and the United States are required in order to assess the impact of atmospheric loadings (pollution burdens), using models and other techniques.

The first pollutant investigated under the LRTAP Program is sulphur and its compounds, and an important aspect of the emission of sulphur compounds is the contribution from natural sources. These sources include water bodies, marshes, volcanic activity, the decay of plant matter, and other biological processes.

The fact that sulphur is emitted into the atmosphere through natural processes has been recognized for at least 35 years (Conway 1942). Interest in the magnitude of these emissions, however, has been heightened by recent evidence that biogenic sulphur sources may make significant contributions to the atmospheric loading of particulate sulphate which can be transported over large distances.

This report is a nationwide inventory of natural emissions of sulphur compounds into the atmosphere and an evaluation of their contribution to the overall sulphur burden of ambient air. Data on estimates of natural emissions were obtained through a literature review. Such data are relatively sparse and in some cases contradictory, making some reported estimates of source emissions quite speculative. The emission estimates presented here are likely to be accurate only to within an order of magnitude and, as such, are considered preliminary and subject to revision.

The principal sulphur compound emitted by biological processes into the atmosphere is hydrogen sulphide. Others detected include carbon disulphide, carbonyl sulphide, dimethyl sulphide, and methyl mercaptan. Forest fires emit sulphur dioxide while sea and lake sprays release sulphates.

The total emissions of sulphur from natural sources in Canada have been estimated at about 500 000 tonnes a year. The total anthropogenic emissions of sulphur are about 2 600 000 tonnes (1976 estimate). The greatest natural sulphur emissions occur on the Atlantic and Pacific coasts and in Ontario and Quebec.

Table 1 provides a regional breakdown of natural sulphur emissions in Canada, by source. These sources and their contribution to the sulphur content of the atmosphere in Canada are summarized in the following pages.

1.1 Soils

Sulphur is released into the atmosphere from soils through two main processes: microbial anaerobic reduction of sulphate, and bacterial methylation. The former produces large amounts of hydrogen sulphide particularly under high moisture conditions. The latter emits methylated organic compounds such as dimethyl sulphide and dimethyl disulphide. The sulphur emissions from soils were estimated from fluxes cited in the literature and applied to soil types in Canada on a census division basis. The estimated annual emissions of sulphur compounds from this source are 246 563 tonnes.

1.2 Aquatic Sources

Hydrogen sulphide is emitted from coastal areas and freshwater lakes by two processes: the decomposition of organically bound sulphur, and the anaerobic reduction of inorganic sulphate. Sulphate reduction to sulphide has been suggested as the predominant process in aquatic systems. Emission rates of hydrogen sulphide vary considerably, the highest occurring in highly productive estuarine ecosystems, swamps and marshes. Aquatic emissions were estimated using measured fluxes applied to various coastal divisions and lake categories of Canada. The estimated sulphur emissions from this source are 63 529 tonnes a year.

1.3 Vegetation

Leaves of trees and herbs emit dimethyl sulphide, but the mechanism is not known. During senescence, leading to the death of leaves, sulphur release rates have been shown to increase 10 to 100 times. The annual sulphur production by vegetation decreases northward and is related to shorter growing seasons and lower summer temperatures. The release from this source is estimated to be 8 907 tonnes a year.

1.4 Sea and Lake Spray

Water droplets from sea and lake surfaces are released into the atmosphere by wave action, creating myriads of bursting bubbles. These water droplets, which subsequently evaporate, contain sulphate along with other chemical compounds prevalent in seawater and lake water. A wind-dependent emission rate for this source was derived and applied to the coastal areas of Canada. An estimated 188 900 tonnes of sea-salt

TABLE 1 SUMMARY OF NATURAL EMISSIONS OF SULPHUR INTO THE ATMOSPHERE IN CANADA
(tonnes of S per year)

Province/Territory	Biogenic Emissions				Other Natural Sources*			
	Soils	Marine	Lakes	Vegetation	Sea Salt SO ₄	Soil Dust	Forest Fires	
Newfoundland	2 187		203	138			81	
Prince Edward Island	72		-	200				
Nova Scotia	609		102	226			3	
New Brunswick	761		100	278			5	
Quebec	23 888	36 692**	1 471	1 772	101 200**		60	
Ontario	65 672	4 381	3 543	2 698			55	
Manitoba	47 860		2 650	552			203	
Saskatchewan	17 217		2 434	1 245			164	
Alberta	31 062		654	1 016			64	
British Columbia	29 515	10 465	810	782	27 300	500****	171	
Yukon	4 950							
Northwest Territories	22 770	92***			60 400****		194	
Canada	246 563	51 631	11 898	8 907	188 900	500	1 000	

Canadian Total - 509 406 tonnes

* Does not include 7 tonnes from lake sulphate.

** Includes Atlantic Provinces and Quebec.

*** Includes Yukon and Northwest Territories.

**** Includes Saskatchewan, Alberta and British Columbia.

sulphate as sulphur are released into the atmosphere annually. Similarly, it is estimated that Canadian freshwater lakes release only about 7 tonnes of sulphur a year.

1.5 Soil Dust

Wind entrainment of dust particles containing sulphur contributes to the atmospheric sulphur burden. Only sparse data are available on production rates of soil dust and the sulphur content of arid soils. The main areas prone to wind erosion are in Alberta and Saskatchewan, with a few pockets in British Columbia. An annual sulphur emission of 500 tonnes is estimated for this source.

1.6 Forest Fires

Sulphur dioxide has been detected during forest fires. Based on estimated fluxes and the average area of forests destroyed by fire in Canada, the annual sulphur emission is estimated to be 1 000 tonnes.

2 ATMOSPHERIC SULPHUR BUDGETS

2.1 Introduction

Global budgets are a means of determining the fluxes and burdens in the sulphur cycle without having to investigate the details of each individual process (e.g., the generation mechanism of reduced sulphur compounds released into the atmosphere from soils). They help in identifying the most significant uncertainties about the circulation of compounds. However, global sulphur budgets have a weakness in that they are an average of extremely diverse conditions found throughout the world. In the following sections the atmospheric reservoir is examined along with those reservoirs that are sources of emissions into the atmosphere. As well, an attempt is made to determine which reduced sulphur compounds are prevalent in the atmosphere.

The global sulphur cycle involves four reservoirs - atmosphere, hydrosphere, lithosphere, and biosphere - and transfers between them. Conway (1942) first determined that the world's rocks contain too little sulphur, by a factor of three, to account for the sulphate delivered by rivers into the ocean. This deficiency implied that three quarters of the sulphur loading of the oceans originates from the atmosphere. Of this amount, about one third, or one quarter of the total budget, was assumed to originate from industrial sources.

To account for the remaining two thirds, or half the total budget, Conway hypothesized that hydrogen sulphide (H_2S) is produced over the shelf areas of the oceans and reaches the atmosphere. This atmospheric sulphur is carried in over land and contributes to the river run-off of sulphur into the oceans, balancing the global sulphur budget. However, despite this hypothesis, Eriksson (1959) noted that it is not certain whether cycled sulphur reaches the land as a sea-spray particle or as a reduced sulphur compound such as H_2S . Using isotope techniques, Jensen (1962) resolved the problem in favour of reduced sulphur compounds. Lighter isotopes of sulphur appear preferentially in reduced compounds such as H_2S . Even if a gaseous reduced compound is oxidized in the atmosphere, the sulphur remains isotopically light. Jensen found that atmospheric sulphate over the oceans contains a smaller proportion of heavy sulphur isotopes than does sulphate in seawater. From this he concluded that a component of the atmospheric sulphate over the oceans does not originate from sea spray but must be formed from reduced sulphur compounds.

2.2 Comparative Sulphur Budgets

There have been various attempts to develop global atmospheric sulphur budgets to determine the relative importance of sulphur sources. These budgets have yielded estimated rates of emission of sulphur into the atmosphere from anthropogenic, sea-spray, biogenic and volcanic sources. Table 2 gives the sulphur fluxes of these sources into the air from data provided by various authors.

TABLE 2 GLOBAL ATMOSPHERIC SULPHUR BUDGETS CONSTRUCTED BY VARIOUS RESEARCHERS

Source	Eriksson (1963)	Junge (1963)	Robinson and Robbins (1970)	Kellogg et al. (1972)	Friend (1973)	Granat (1976)
	Tg S/yr					
Pollution	40	40	70	50	65	65
Biological Decay						
Land	110	70	68		58	
Marine	170	160	30	90	48	32
Sea Spray	45	*	44	43	44	44
Volcanos	-	-	-	1.5	2	3
Soil Dust	-	-	-	-	-	0.2
Total Emissions into Atmosphere	365	315	212	184.5	217	144.2

* Junge's model was for excess sulphur only, so the sea-salt component was not included.

Although the estimated source fluxes vary widely in their relative contributions to the global budget, the greatest controversy centres on the contribution of biogenic sources which produce the reduced compounds necessary to balance the budget. Granat (1976) used a production rate of 5 Tg S/yr of dimethyl sulphide (DMS) (estimated by Hitchcock 1975) from land and marine sources and added 27 Tg S/yr of other natural sulphur compounds to balance his budget.

The estimates of biogenic emissions have trended downwards over the years (Table 2), a trend supported somewhat by experiments. Nriagu and Coker's (1978) isotope

composition measurements of sulphur in precipitation indicated that biogenic release of sulphur may be considerably smaller than suggested in most budgets. Jaeschke et al. (1978) interpreted their H_2S flux results as being unable to support present global biogenic estimates. Hitchcock (1975), using fluxes measured by Lovelock et al. (1972), estimated that DMS emissions into the atmosphere contribute only about 2 to 5 Tg S/yr.

Several important observations and conclusions can be made from the present status of global atmospheric budgets:

1. Biogenic emission estimates vary with changes in contribution from anthropogenic, sea-spray and volcanic sources because of back-calculation techniques;
2. In recent years, emission estimates from biogenic sources have generally decreased in magnitude;
3. H_2S and DMS do not appear to account for the bulk of biogenic emissions; other reduced organic sulphur compounds may be required to balance the atmospheric sulphur budget;
4. The relative contributions from land and sea biogenic sources vary greatly.

Recently, researchers re-examining sulphur budgets have found inconsistencies indicating that the biogenic emissions may be as large as originally estimated by Junge (1963) and Eriksson (1963). Nochumson (1979) noted errors in the budget by Robinson and Robbins (1970) that caused them to underestimate the contribution from biogenic sources by 44 Tg S/yr. Correcting these errors increases their budget's biological decay component from 118 Tg S/yr to 162 Tg S/yr.

Hitchcock (1978) re-estimated natural sulphur releases from the oceans on the basis of total sulphate in river discharge, corrected for rock weathering, anthropogenic releases, and volcanic and hydrothermal sources. Her figures indicate a sulphur release of about 200 to 250 Tg S/yr (including sea salt) from the oceans, which is similar to the estimates of early workers in the field (cf Eriksson (1963) and Junge (1963) in Table 2).

Because these budget estimates are so uncertain, in some cases within an order of magnitude, they are of little use in determining the magnitude of natural emissions in Canada. However, an attempt was made by Katz (1977) to derive a sulphur budget for Canada on the basis of the Kellogg et al. (1972) global budget. Katz estimated that biogenic sources and sea salt release 5.02 and 1.7 Tg S/yr, respectively, into the Canadian atmosphere.

2.3 Atmospheric Concentrations

Representative background concentrations for reduced sulphur compounds, carbonyl sulphide (COS), sulphur dioxide (SO₂), and particulate sulphate (SO₄) are given in Table 3. Data are still sparse for H₂S and organic sulphur compounds because until recently no techniques were available for reliable sampling and detection at the very low concentrations existing in the atmosphere.

The reported background concentrations of H₂S over land are generally larger than those over marine areas, supporting the hypothesis that land surfaces contribute more H₂S to the sulphur budget. Meszaros (1978), reviewing atmospheric concentration data, assumed an average H₂S global concentration of 0.14 µg S/m³.

Only two measurements of COS concentrations have been made: 0.27 µg S/m³ and 0.67 µg S/m³ (Hanst *et al.* 1975, Sandalls and Penkett, 1977). Sandalls and Penkett (1977) observed an average concentration of 0.42 µg S/m³ for carbon disulphide (CS₂). No measurements of background concentrations of methyl mercaptan (CH₃SH) have been made, but Sandalls and Penkett (1977) suggest a concentration of 0.005 µg S/m³ based upon Cox's (1975) estimated residence time of 0.09 days (section 2.4). Maroulis and Bandy (1977) measured DMS concentrations of about 0.07 µg S/m³ off the Atlantic coast of the United States.

The data on concentrations of SO₄ and SO₂ (to a lesser extent) are provided to illustrate possible concentrations maintained by H₂S or other natural gaseous sulphur compounds.

The precursor of a portion of the background SO₂ is likely to be natural sulphur gases (section 2.4). However, the relative contribution of natural gaseous compounds to SO₂ concentrations cannot be inferred directly from Table 3. The short and variable residence times of gaseous sulphur preclude the attainment of a steady-state condition. The existence of lower SO₂ concentrations over the oceans, compared with those observed over land, might indicate a lower production of precursor gases. However, seawater is an SO₂ sink (Liss and Slater 1974) which might account entirely for the lower SO₂ concentrations over the oceans.

Investigations by Gravenhorst (1976) into the composition of SO₄ particles in unpolluted air over the oceans have shown that the SO₄ concentration of aerosols in marine air is always in excess compared with the SO₄ concentration of ocean water. The contribution of non-maritime SO₄ to total atmospheric SO₄ over the oceans is 60-80%. Reported concentrations of excess SO₄ have ranged from less than 0.006 µg S/m³ over

TABLE 3 BACKGROUND CONCENTRATIONS OF SULPHUR COMPOUNDS ($\mu\text{g S/m}^3$)

Terrestrial	Marine	Assumed Global Average
Hydrogen Sulphide (H_2S)		
0.13 - 0.4	Wales Smith et al. (1961)	0.26
0 - 0.4	Panama Axelrod et al. (1969)	0.23
0.03 - 0.09	Colorado Natusch et al. (1972)	0.14
0.10 - 0.26	Illinois and Missouri Breeding et al. (1973)	
0.09	Rhine-Main Georgii (1978)	
	Barbados, Sal.Is. Slatt et al. (1978)	Robinson and Robbins (1968)
	Southern Florida Slatt et al. (1978)	Friend (1973)
	North Sea Georgii (1978)	Meszaros (1978)
	North Sea Jaeschke (1977)	
Carbonyl Sulphide (COS)		
0.27	North Carolina Hanst et al. (1975)	
0.67	England Sandalls and Penkett (1977)	
Carbon Disulphide (CS_2)		
0.42	England Sandalls and Penkett (1977)	
Methyl Mercaptan (CH_3SH)		
		0.005
		Sandalls and Penkett (1977)
		(from residence time to contribute 70 Tg S/yr to atmosphere)

TABLE 3 BACKGROUND CONCENTRATIONS OF SULPHUR COMPOUNDS ($\mu\text{g S/m}^3$) (continued)

Terrestrial	Marine	Assumed Global Average
Dimethyl Sulphide (DMS)		
	0.07 - 0.08	Atlantic Maroulis and Bandy (1976)
Sulphur Dioxide (SO_2)		
0.5 - 1.7	0.09	N. Atlantic
0.4 - 1.4	0.05	Prahm et al. (1975)
0.4		S. Pacific
		up to 1.7
0.25	nil	Ocean Georgii (1978)
	0.25	Land Granat (1976)
	0.03 - 1.5	Nguyen et al. (1974) 0 - 5° N. Atlantic Atlantic Georgii (1978) (probably contains anthropogenic SO_2) 30 - 60° N. Atlantic Meszaros (1978)
Excess Sulphate (SO_4)		
<0.3	0.1 - 0.5	Atlantic
0.17	0.04 - 0.1	Gravenhorst (1978)
1-3		Pacific
	0.14	Gillette and Blifford (1971)
	0.3*	N. Atlantic
	0.006*	Prahm et al. (1975)
		S. Pacific
		Indian Ocean
		Meszaros and Vissy (1974)
		1 - 2
		0.6
		0.1 - 0.5
		0.1 - 0.5
		N. Hemisphere Castleman et al. (1974)
		S. Hemisphere Granat (1976)
		Land Granat (1976)
		Ocean Granat (1976)

* uncertain estimate based on particle size number frequency distributions.

the Indian Ocean (Meszaros and Vissy 1974) to $3 \mu\text{g S/m}^3$ over rural land areas (Meszaros 1978).

Excess sulphate may have gaseous precursors such as DMS emanating from the oceans. If this is the case, the measurements of Meszaros and Vissy (1974) support a higher production of reduced sulphur compounds in warm waters near the equator. Unlike the case of SO_2 , there is no discernible difference between SO_4 concentrations over land and oceans.

2.4 Fate of Sulphur Compounds in the Atmosphere

The sulphur compounds in the atmosphere emitted from natural sources may include H_2S , SO_2 , DMS, DMDS and CH_3SH . The generally accepted hypothesis is that reduced sulphur compounds introduced into the atmosphere are oxidized to sulphates, with SO_2 as a possible intermediate. The residence times and removal mechanisms of various compounds are given in Table 4.

The rate of production and the atmospheric residence time of natural sulphur compounds are most commonly estimated by the application of a steady-state model in which rates of production and removal are equal. Assuming that the removal process is a first-order kinetic process, the atmospheric residence time is given by:

$$\tau = \frac{C_s}{R} \cdot M \quad (1)$$

where: τ = atmospheric residence time

C_s = average concentration of sulphur compound

R = rate of production

M = mass of the atmosphere.

Junge (1963), Friend (1973), Kellogg et al. (1972) and Slatt et al. (1978) have used this equation to estimate the atmospheric lifetime of H_2S (Table 4). However, Slatt et al. (1978) have pointed out limitations in this approach. First, the assumption of a steady-state concentration is tenuous. Even if the average concentration of H_2S in the atmosphere is constant, it does not represent a steady state in terms of chemical kinetics. Second, some transformation reactions, such as H_2S reactions with ozone (O_3) and hydroxyl radicals (OH) (Table 4), are not first-order reactions and are incompatible with equation 1. As an example of the possible inaccuracy inherent in assuming a first-order kinetic approximation, a global H_2S production of about 430 Tg S/yr is obtained if an atmospheric residence time of 0.5 days (Jaeschke et al. 1978) and an average concentra-

TABLE 4 ATMOSPHERIC RESIDENCE TIMES OF NATURAL SULPHUR COMPOUNDS

Reference	Residence Time	Remarks
Hydrogen Sulphide (H_2S)		
Cox (1975)	2.3 days	reaction with OH radicals
Jorgensen (1977)	1-5 days	
Kellogg <u>et al.</u> (1972)	<1 day	global sulphur budget
Junge (1963)	1.7 days	global sulphur budget
Friend (1973)	3.5 days	global sulphur budget
Cadle and Ledford (1966)	2 hours	based on experimentally determined reaction rates $\text{H}_2\text{S} + \text{O}_3 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$ in the presence of aerosols
Slatt <u>et al.</u> (1978)	terrestrial 10-32 hours	based on Friend's estimates of H_2S production and concentrations measured in study
	marine 4-35 hours	
	global 7-33 hours	
	a few minutes	based on Cadle's reaction rates and measured concentrations; suggested as "improbable"
Stuhl (1974)	30 hours	reaction with OH radical at concentration of 2.3×10^6 molecules/cm ³
Jaeschke <u>et al.</u> (1978)	12.2 hours	reaction with OH radical and measured H_2S concentrations
Carbon Disulphide (CS_2)		
Sandalls and Penkett (1977)	1 year	based on reaction with OH radicals and measured concentrations
Dimethyl Sulphide (DMS)		
Cox (1975)	0.8 days	based on reaction with OH radicals
Lovelock <u>et al.</u> (1972)	7 days	suggested but not supported by any evidence
Methyl Mercaptan (CH_3SH)		
Cox (1975)	0.09 days	based on reaction with OH radicals
Carbonyl Sulphide (COS)		
Sandalls and Penkett (1977)	20 years	based on reaction with OH radicals

tion of $0.14 \mu\text{g S/m}^3$ (Meszaros 1978) are substituted in equation 1. This rate is double the biogenic release rates estimated by Junge (1963) and Eriksson (1963) (Table 2).

2.4.1 Transformation Mechanisms and Residence Times. Oxidation of H_2S can proceed in cloud water droplets or in a homogeneous process such as a reaction with O_3 . Although the oxidation of H_2S in solution may proceed quite rapidly in cloud or fog water droplets (Penkett 1972), the decay rate in this process is probably small compared with that of other mechanisms (Granat 1976). Ozone, oxygen atoms (O), molecular oxygen (O_2) and OH radicals may all react with H_2S .

Cadle and Ledford (1966) found that there is a rapid reaction between O_3 and H_2S in the presence of aerosols. However, Hales *et al.* (1974), who critically examined the estimated oxidation rate of H_2S , concluded that this mechanism results in a global H_2S lifetime of several weeks.

On a local basis, Hitchcock (1977) found that the highest SO_4 concentrations occur on days when O_3 is transported downward from the upper troposphere and lower stratosphere. Her analysis indicated that much of the SO_4 present appears to be from local biogenic sources associated with the distribution of wetlands. These observations support a relatively short H_2S lifetime in the presence of increased concentrations of O_3 . According to Hitchcock *et al.* (1978), under certain conditions SO_2 is derived from the precursor H_2S and an unknown proportion of SO_4 appears to be of biogenic origin.

Stuhl (1974) and Cox (1975) estimated the reaction rate of H_2S with OH in the atmosphere. They arrived at atmospheric H_2S lifetimes of 1.3 and 2.3 days, respectively. Jaeschke *et al.* (1978), using Stuhl's (1974) reaction rates and their own measured concentrations of H_2S , estimated the residence time to be about 0.5 days. Most of the recent evidence suggests a residence time of less than one day on a global basis and, in some circumstances, such as in the presence of elevated O_3 concentrations, possibly in the order of a few hours or less.

Cox and Sandalls (1974) concluded that DMS is oxidized directly to SO_4 by OH radicals and estimated a residence time of 0.8 days (Cox 1975). The concentrations of DMS and H_2S (Table 3) and their respective residence times in the atmosphere appear comparable; if so, it suggests that the production rates of DMS and H_2S are also comparable, at least over the oceans.

COS and CS_2 have relatively long residence times in the atmosphere (Sandalls and Penkett 1977), in contrast to a two-hour lifetime estimated for CH_3SH (Cox 1975). According to Sandalls and Penkett (1977), CH_3SH has only to be available in concentra-

tions in the order of $0.005 \mu\text{g S/m}^3$ to account for 70% of the natural turnover of sulphur in the atmosphere. COS is possibly generated in the atmosphere by photolysis of CS_2 (Sandalls and Penkett 1977) or from natural land or marine sources (Adams 1978).

From available information, the following observations are of paramount importance in attempting to estimate sulphur fluxes from natural sources:

- H_2S lifetimes in the atmosphere could conceivably vary from a few minutes to a few days depending on the dominant transformation mechanism;
- CH_3SH may have a very short lifetime in the atmosphere and could balance the atmospheric sulphur budget if present in concentrations of $0.005 \mu\text{g S/m}^3$;
- current observed concentrations support the hypothesis that the evolution of H_2S from natural sources balances the atmospheric sulphur budget if H_2S has a residence time comparable to that of CH_3SH , or shorter;
- production rates or residence times or both, estimated in global budgets, assuming a steady state, are not accurate.

The actual H_2S reactions in the atmosphere must be determined before accurate indications of H_2S production can be obtained from measurements of this compound in the atmosphere.

3 GENERATION MECHANISMS AND FLUXES OF NATURAL ATMOSPHERIC SULPHUR

3.1 Biogenic Sources

3.1.1 Terrestrial Processes. In most well-drained soils, sulphur is present predominantly in the SO_4 and organically combined forms. Sulphur content varies considerably among regions and soil types. In Manitoba, chernozems have a low sulphur content, and in fact may be sulphur deficient. Luvisols in Manitoba and Ontario are also frequently sulphur deficient.

Losses of sulphur from soils into the atmosphere have been known for some time, although the mechanisms have not been studied in detail. Siman and Jansson (1976b) showed losses of sulphur over a 35-day period varying from 0.02 g S/m^2 for unfertilized soils, to between 0.2 and 0.3 g S/m^2 for fertilized soils. The presence of plants increased the evolution of sulphur.

Natural sulphur losses occur indirectly through microbial anaerobic reduction of SO_4 as well as directly from living, senescent and decaying vegetation. Methylation and other bacterial mineralization processes can occur rapidly during the breakdown of soil organic matter and appear to account for much of the sulphur losses from anaerobic soils.

Releases from luvisols and brunisols, recorded by Adams (1978a), Hitchcock (1975), and Lovelock *et al.* (1972), included methylated organic compounds such as DMS and DMDS. H_2S , CS_2 and COS were also produced. More-limited information is available for podzols and chernozems (Adams 1978c), but similar compounds appeared to be evolved.

From the meagre data available, it appears that all terrestrial soils can produce a variety of volatile organic sulphur compounds, and no consistent differences have been reported. All soils, when wetted or under high moisture conditions, produce larger amounts of H_2S . Under these conditions, organic sulphur emissions may be suppressed.

Lovelock *et al.* (1972) presented data from laboratory experiments on the emission of DMS from a variety of soils collected throughout the United States. No other soil information was given. Emission rates per gram of soil varied from 21×10^{-9} to $84 \times 10^{-9} \text{ mg/h}$. DMS production decreased in sealed flasks as CO_2 concen-

trations increased; this may suggest lower DMS evolution in anaerobic soils in the presence of higher concentrations of CO_2 .

Adams (1978b) showed that most terrestrial soils produce some H_2S even at field capacity (i.e., normal moisture conditions). In loams, silt loams and clay silts, it is produced in amounts similar to those of organic sulphur compounds. H_2S , DMS and DMDS fluxes from luvisols were an order of magnitude higher than those from brunisols. Brunisols produced more COS according to Adams *et al.* (1978a) than did other soil types. However, the maximum COS- CS_2 flux of $3.1 \text{ mg S/m}^2/\text{yr}$ was from brunisols and contrasts with $21.5 \text{ mg S/m}^2/\text{yr}$ from the marine sediment Cove Sound sampling locations. Data from Adams *et al.* (1978a) are summarized in Table 5.

TABLE 5 SULPHUR FLUXES FOR VARIOUS SOILS ACCORDING TO MEAN TEMPERATURE

Mean Temperature (°C)	Total S ($\text{mg S/m}^2/\text{yr}$)	Soil Type	Flux ($\text{mg S/m}^2/\text{yr}$)				
			H_2S	DMS	DMDS	COS	CS_2
13	1.39	Alluvial Clay	0.14	0.05	-	1.2	-
17	7.66	Luvisol	1.5	1.5	3.4	0.3	0.96
12	5.15	Brunisol	0.27	0.13	1.7	2.2	0.85
12	3.4	Organic	-	0.6	0.1	2.0	0.7

Fluxes of DMS and DMDS were highest in luvisolic soils; however, these soils had the highest ambient temperatures, which may explain some of the differences. These data confirm the findings of Hill *et al.* who showed extremely low H_2S emissions at temperatures below 10°C . Nighttime and daytime differences were also attributed, at least in part, to temperature. Although data are inadequate for significant conclusions, it appears that some trends are emerging, with higher DMDS and lower COS fluxes recorded during daytime.

Total sulphur fluxes for different soil types are lacking in the literature. The most comprehensive studies were done by Adams *et al.* (1978a, b and c), who showed a wide range in fluxes (Table 6).

Most of Adams's work has dealt with soils that appear to be under some form of cultivation. Higher fluxes have been recorded by Siman and Jansson (1976a and b) in a

TABLE 6 SULPHUR FLUXES FOR VARIOUS SOILS

Soil	Flux (mg S/m ² /yr)	Source
Luvisols	5.7 - 8.4	Adams (1978 a)
	16.9 - 17.0	Adams (1978 b)
	17.0 - 58.0	Adams (1978 c)
Brunisols	3.0 - 5.1	Adams (1978 a)
	7.1 - 8.2	Adams (1978 b)
	8.0 - 90.0	Adams (1978 c)
Podzols	13.0	Adams (1978 c)
Chernozems	120.0	Adams (1978 c)
Organic terrain	0.0 - 3.4	Adams (1978 a)

series of pot experiments, but it is unclear how these can be related to field conditions. They recorded fluxes of 20 mg S/m²/35-day period under unfertilized conditions and about 200 mg S/m²/35-day period under conditions of high sulphur fertilization. Siman and Jansson's work would suggest that values for the Prairies, particularly Manitoba, could be underestimated in this study by an order of magnitude.

3.1.1.1 Aerobic processes in soils. The majority of volatile organic sulphur compounds are produced by aerobic methylation processes. DMS and DMDS have been detected in a wide variety of well-drained soils by Adams *et al.* (1978c), and are probably formed by methylation (Lovelock *et al.* 1972, Challenger 1951). CS₂ and COS appear to be produced largely as breakdown products from proteins containing cysteine and cystine, although other processes may be involved (Banwart and Bremner 1975).

3.1.1.2 Anaerobic processes in soils. The principal processes leading to the production of gaseous sulphur compounds under anaerobic conditions involve the reduction of sulphate to H₂S by strains of the bacteria *Desulfovibrio* and *Desulfotomaculatum*. Jorgensen (1977) and Hansen *et al.* (1978) have shown that some H₂S (3%) originates from the decomposition of organic sulphur.

The behaviour of sulphate-reducing bacteria in a wide variety of soils is well known (Hitchcock and Wechsler 1972). There are data for muds, swamps, fens, marshes, bogs and periodically flooded lands (Burgeff 1961, Connell and Patrick 1968, Engler and Patrick 1973, Jorgensen 1977, Sparling and Hennick 1974, Takai and Kamura 1966, Vamos 1964, and others). These workers have shown that the release of H₂S from soils depends

on the oxidation-reduction (redox) state, acidity, the supply of short-chain organic compounds and the soluble iron concentration.

H_2S concentrations showed a marked seasonal pattern, high from May to July, then decreasing through late summer and fall. They peaked just below the soil surface and in some cases exceeded 15 mg H_2S /100 g of fresh soil (Hennick 1971, Sparling and Hennick 1974). Jorgensen (1977) also showed that peak sulphate reduction occurred 1-4 cm below the surface of waterlogged sediments and that up to 10% of the H_2S was precipitated as iron sulphides and not emitted into the atmosphere.

Metal sulphides appear to be relatively stable in anaerobic soils, with iron and manganese least stable (Engler and Patrick 1975). However, it has been reported that concentrations greater than 2 000 ppm are required before significant loss into the atmosphere occurs (Harter and McLean 1965).

The behaviour of hydrogen and metal sulphides is closely related to redox conditions. Harter and McLean (1965) showed that sulphide-producing organisms become active at a redox of -75 mV and active growth occurs at -200 mV. Connell and Patrick (1968) showed that redox conditions of -150 mV are required for sulphide accumulation. These conditions occur only in gleysols and some organic soils. The oxidizing nature of the upper portions of gleysols may preclude large emissions of H_2S .

Connell and Patrick (1968) reported sulphide production from soils between pH 5.5 and 9.5. A review of other sources indicated some production between pH 4.2 and 10.4; however, significant accumulation of sulphide probably does not occur below a pH of 6.0. This would seem to indicate that acid fibrisols, which have pH values between 3.6 and 4.6, are not major sources of H_2S .

In summary, it appears that while waterlogged organic soils have a high potential for sulphur emission, edaphic conditions frequently preclude the evolution of large amounts of H_2S . Increased acidity in mesisols and fibrisols and the fixing or oxidation of H_2S act to reduce sulphur emission rates. Sulphur production decreases below 10°C and reaches significant levels only above 20°C. This would suggest low sulphur production in cryoboreal, sub-arctic and arctic soil climates.

Wetlands, marshes and reed swamps probably have fluxes of between 1 and 30 mg $\text{S}/\text{m}^2/\text{yr}$. Muck soils in eutrophic wetlands have high fluxes averaging between 2 and 15 mg $\text{S}/\text{m}^2/\text{yr}$, higher still under conditions of rapid decomposition. Soils with a high fines content frequently have lower recorded fluxes of 1 - 3 mg $\text{S}/\text{m}^2/\text{yr}$, possibly because of slow diffusion rates and re-oxidation or fixation by iron or manganese.

Many wetland soils are distributed in the northern boreal or cryoboreal soil climates and are thus low-producing sites. Acid peats (fibrisols) produce small amounts of sulphur -- 0 - 4 mg S/m²/yr -- although the local dominance of this soil type may lead to a higher ranking.

3.1.2 Aquatic Processes. In most oxygenated waters, sulphur is present primarily as SO₄, in concentrations ranging from less than 1 mg/L in lakes with low electrolyte levels, to in excess of 50 000 mg/L in SO₄ saline lakes. As such, the main release of sulphur into the atmosphere from lakes could be regarded as being derived from evaporated spray during high wind conditions. The traditional theory also holds that biogenic emission of H₂S is a more significant source.

Such H₂S may be generated by two mechanisms: the decomposition of organically bound sulphur, and the anaerobic reduction of inorganic SO₄. Although Rasmussen (1974) indicated that considerable release occurred from organic sulphur, Hansen *et al.* (1978), Jorgensen and Cohen (1977) and others presented strong evidence that sulphate reduction to sulphide is the predominant process in aquatic systems. This process occurs rapidly under anaerobic conditions, but may also take place in aerobic sediments in small anaerobic interstices.

The decomposition of organically bound sulphur produces a variety of volatile sulphides, including DMS, DMDS, CH₃SH and probably small amounts of CS₂ and COS (Adams *et al.* 1978a). Other organic sulphides and mercaptans have been tentatively identified but their chemical structures have not been confirmed (Adams personal communication).

Few data on organic sulphur compounds are available. DMS was not detectable in air but was measured at a concentration of 1.2×10^{-5} mg/m³ in the Atlantic Ocean off the coast of England (Lovelock *et al.* 1972). Atmospheric measurements of other volatile compounds have received less attention because of short residence times and extremely low concentrations.

Most research has been oriented toward measurements of emission rates and fluxes. Information is available for exchanges across sediment-water, sediment-air and water-air interfaces. Estimates of rates of emission of sulphur into the atmosphere vary considerably among researchers owing to variations in experimental techniques and test environments.

Factors causing variations in emission rates are numerous. They include air and surface temperatures, wind speed, atmospheric ventilation (Hitchcock 1977), vertical

mixing, concentration gradients, diffusion rates and gas solubilities, oxygen concentrations in water, water depth overlying the anaerobic layer, light (photosynthesis level) and the rate of sulphate reduction. Adams *et al.* (1978b) showed that the flux changed from 0.03 to 7.0 g S/m²/yr as a result of the temperature increasing from 17.5°C to 34°C. Zero emissions are characteristic of snow and ice cover. Seasonal emissions vary largely with mean temperature.

Biogenic sulphur emissions are related to primary production (Hitchcock 1975), either by the aerobic production of methylated sulphur forms during normal metabolism, or by H₂S and DMS production during anaerobic decomposition of organic residues.

In aerobic waters, H₂S is rapidly oxidized to SO₄ and therefore does not normally occur in significant concentrations. H₂S may also be reoxidized to SO₄ in the upper sediment layers by aerobic bacteria and algae. Release of H₂S into the atmosphere is virtually nil if anaerobic sediments or anoxic hypolimnetic conditions are overlain by oxygenated water. Recent studies have indicated that a 10-cm water layer almost completely stopped H₂S release into the atmosphere (Jorgensen 1977). In lakes and oceans, it appears that only under conditions of strong vertical water movement would H₂S be released into the atmosphere from anaerobic bottom waters.

The general conclusion from these studies is that H₂S is released from oxygen-deficient waters, from wet areas with only 2-5 cm of water cover, from exposed sediments, and from turbulent littoral or coastal regions.

Measurements of H₂S values in the air or at the air-water interface have been limited because of the extremely low concentrations and problems in sampling and detecting them. Junge (1963) reported atmospheric concentrations ranging from 2 to 20 µg/m³ for near-shore marine areas, while above polluted marine shorelines they approached the odour limit of 200 µg/m³. Georgii (1976) recorded concentrations of 0.6 µg/m³ at the surface of a shallow estuarine area -- which decreased to 0.1 - 0.2 µg/m³ at a height of one metre -- and 0.38 µg/m³ in seawater.

Fluxes for H₂S vary considerably, the highest being in highly productive estuarine ecosystems, swamps and marshes. Adams *et al.* (1978a) measured fluxes in marine coastal areas which included exposed mudflats, estuarine swamps and marshes. The recorded H₂S fluxes ranged widely:

<u>Flux (mg S/m²/yr)</u>	<u>Author</u>
1.75 - 44.2 x 10 ⁴	Hansen <i>et al.</i> (1978b)
19.4	Adams <i>et al.</i> (1978b)

24.5 - 33.3

Georgii (1976)

 6.44×10^4 Adams et al. (1978a) 1.39×10^5 Adams et al. (1978b)

Estimates of DMS fluxes are much less variable in marine coastal areas. Several authors have shown a variation between 3.8 and 14.4 mg S/m²/yr. Estimates for other volatile sulphur compounds are generally restricted to the work of Adams et al. (1978a and b). This is a serious data gap because comparisons are not possible. Adams's techniques are being questioned by other workers (Hitchcock personal communication). Fluxes for COS and CS₂ combined in intertidal zones have been recorded by Adams et al. (1978a) as 7.1 mg S/m²/yr although another test gave a reading of 1.2 mg S/m²/yr.

From the available information, it seems that while considerable amounts of volatile organic compounds such as DMS and DMDS have been identified as originating from algae, marine and freshwater ecosystems, measured fluxes of up to 15 mg S/m²/yr indicate that these compounds play a secondary role to H₂S (up to 4.4×10^5 mg S/m²/yr). Littoral and shoreline areas probably are the major aquatic sulphur source. Mechanisms may involve the movement of surface sediments by wave action and subsequent deposition on rocks or beaches where rapid loss of sulphur compounds into the atmosphere could occur. Hypolimnetic sulphur is unlikely to be transferred into the atmosphere except during fall overturn or during winter storms. No seasonal field observations are available yet.

3.2 Other Natural Sources

3.2.1 Sea Spray. Seawater contains about 2.5 mg SO₄/g H₂O. Particles of sea salt formed by the breaking of bubbles have been identified as a major natural source of atmospheric sulphur. Myriads of bubbles, generated mainly by the entrainment of air by white caps and wavelets, eject small droplets into the atmosphere immediately above the sea surface. If these droplets are less than 20 or 30 μm in diameter, they will remain airborne long enough to be evaporated as aerosols. Eriksson (1960) estimated that the annual global production of SO₄ is 44 Tg, 10% of which passes over land.

Sea salt contributes significantly to precipitation sulphate concentrations in coastal areas. Sulphates of precipitation can be divided into components of probable sea and non-sea origin by using the bulk sea ratio SO₄/Na = 0.25 (Sverdrup et al. 1949). Assuming that neither Na nor SO₄ from the ocean is lost preferentially, the sea-salt SO₄ can be determined from the bulk sea ratio if the Na concentration is known.

The relative percentage contributions of sea-salt SO_4 to total SO_4 of precipitation in Canada are listed by province in Table 7. The sea-salt SO_4 fraction in the coastal provinces is substantially larger than in the continental interior. In Ontario and Quebec, there are substantial amounts of precipitation sulphate from anthropogenic sources (Berry 1979), which also reduces the relative contribution of sea-salt sulphates. In northern Ontario, the relative contribution of sea-salt sulphate on an annual basis is about 6%, while in southern Ontario it is about 1%.

TABLE 7 PERCENTAGE CONTRIBUTION OF SEA-SALT SULPHATE TO TOTAL SULPHATE IN WET DEPOSITION*

Province	Annual	Dec.-Feb.	Mar.-May	June-Aug.	Sept.-Nov.
Newfoundland	12	23	10	3	12
Nova Scotia	16	31	16	4	17
New Brunswick	10	29	9	1	6
Quebec	6	11	6	2	3
Ontario	3	9	2	2	3
Manitoba	3	4	2	2	3
Saskatchewan	8	18	4	6	6
Alberta	5	11	6	2	3
British Columbia	13	20	10	5	15

* Based on data from the Canadian Network for Sampling Precipitation (CANSAP) Project for the period April 1977 - March 1978.

As expected, the rate of sea-salt sulphate production is highly dependent on wind speed (Toba 1965, Woodcock 1953). In the coastal provinces, larger contributions to the sea-salt sulphate fraction occur during the winter. During winter there is increased cyclonic activity both in the Maritimes and off the coast of British Columbia, accompanied by higher wind speeds and subsequent increased sea-salt production.

The removal of sea-salt particles from the atmosphere has been measured at various distances inland. Lodge (1955) reported greater than tenfold decreases in sea-salt-particle concentrations 160 km inland from the coast of Puerto Rico. Tsimogami (1975) showed a 50% decrease in concentrations 20-25 km inland from the coasts of Japan. The removal of sea-salt particles as they are advected inland occurs by either wet

or dry deposition. In England, Martin and Barber (1978) found sulphate sea-salt aerosols contributed similar amounts, under dry and wet conditions, to inland deposition gauges, but a much greater amount in wet conditions at coastal locations. The relative amount of deposition in wet and dry conditions varies according to the climate.

The sea-salt-sulphate concentrations observed over the oceans and land are presented in Table 8.

TABLE 8 SEA-SALT-SULPHATE CONCENTRATIONS IN AIR OVER THE OCEANS AND LAND

Reference	SO ₄ Concentration	Location	Comments
Gravenhorst and Jendrieke (1974)	1) 0.01-0.07 $\mu\text{g}/\text{m}^3$ 2) 0.2 $\mu\text{g}/\text{m}^3$ 3) 0.5 $\mu\text{g}/\text{m}^3$	N. Atlantic Ocean	Measured concentrations at 15-m height: 1) at wind force 3 2) at wind force 4 3) at wind force 5.5. Sea-salt sulphate concentrated in 1-10 μ radius particle size
Gillette and Blifford (1971)	0.7 $\mu\text{g}/\text{m}^3$	Pacific Ocean	near-surface concentration may contain "excess" SO ₄
Friend (1973)	0.77 $\mu\text{g}/\text{m}^3$	all oceans	average estimated global concentration
	0.19 $\mu\text{g}/\text{m}^3$	land	average estimated global concentration
Granat (1976)	0.1-0.5 $\mu\text{g}/\text{m}^3$	N. Atlantic Ocean	clean ocean background

Sulphate concentrations except those by Gravenhorst and Jendrieke (1974) usually contain excess sulphate attributable to either natural or anthropogenic gaseous precursors, with values ranging from 0.4 to 1.4 $\mu\text{g}/\text{m}^3$ (Gravenhorst 1978). Gravenhorst and Jendrieke's (1974) data show larger sea-salt-sulphate concentrations with increasing

wind speed. To obtain an estimate of sea-salt-sulphate production as a function of wind speed, relationships developed for sea-salt production rates were scaled by the bulk sea ratio. The following is a description of the estimation procedure:

Toba (1965) used data from Durbin and White (1961) and Woodcock (1953, 1957) to calculate the wind dependence of sea-salt production. For sea-salt particles of mass $1 \times 10^{-9.5}$ g, Toba determined the following sea-salt production rates:

$$\begin{aligned} \log F &= 0.05V - 1.56 & V \geq 9 \\ F &= 0.08 & \text{for } V=7 \\ &= 0.058 & \text{for } V=6 \\ &= 0.02 & \text{for } V=4 \end{aligned}$$

where: F is the production rate in $\text{cm}^{-2}/\text{sec}$

V is the wind speed in m/sec

A particle mass of $1 \times 10^{-9.5}$ g corresponds to an aerosol radius of about 2 to 4 μm , the size interval in which most of the sea-salt-sulphate mass is found (Gravenhorst 1974). The residence time of aerosols in this size range is greater than 6-12 hours (Toba 1965). Toba did not obtain values for wind speeds of less than 4 m/sec. A rough approximation may be obtained for 3 m/sec by assuming that the ratio of observed concentrations is proportional to the rate of production at different wind speeds. Using this value and sea-salt concentrations determined by Lovett (1978) during light wind observations, sea-salt production at a wind speed of 3 m/sec (11 km/h) is estimated to be about $0.015 \text{ cm}^{-2}/\text{sec}$.

The proportion of seawater sulphate can now be estimated from the sea-salt production rate as sodium by scaling the flux by the bulk sea ratio. Using these assumptions, estimates of sea-salt sulphate fluxes were determined for various wind speeds (Table 9).

Large freshwater lakes may also emit SO_4 particles into the air by the same mechanism as oceans. However, no observations of particle production from freshwater lakes by the bursting bubble mechanism have been made. An approximation of the SO_4 production rate can be obtained by scaling the sea-salt-sulphate production rates by the ratio of the lake SO_4 concentration to seawater SO_4 concentration. The lake production rate can then be calculated using the following formula:

$$F_{\text{Lake SO}_4} = \frac{\text{SO}_4 \text{ Lake}}{\text{SO}_4 \text{ Seawater}} \times F_{\text{Sea SO}_4}$$

where: $F_{\text{Sea SO}_4}$ = sea-salt-sulphate production rate
 $\text{SO}_4 \text{ Lake}$ = sulphate concentration in lake water
 $\text{SO}_4 \text{ Seawater}$ = sulphate concentration in seawater

TABLE 9 SEA-SALT-SULPHATE FLUXES AS A FUNCTION OF WIND SPEED

Wind Speed		Sea-Salt Particle Production Rate	Sea-Salt-Sulphate Flux	
m/sec	km/h		mg $\text{SO}_4/\text{m}^2/\text{day}$	mg S/ m^2/day
3	11	0.015	0.41	0.14
4	14	0.02	0.54	0.18
5	18	0.035	0.95	0.32
6	22	0.058	1.56	0.52
7	25	0.08	2.16	0.72
10	36	0.09	2.44	0.81
15	54	0.15	4.06	1.35
20	72	0.27	7.34	2.45

3.2.2 Volcanos and Hot Springs. The sulphur compounds emitted by volcanos are predominantly SO_2 and H_2S , along with smaller amounts of SO_3 and various other sulphates. Thermodynamic considerations of equilibria existing in magmas suggest that gaseous sulphur must be present largely as SO_2 and H_2S (Naughton *et al.* 1963). The ratio of SO_2 to SO_4 in a primary fumarole often approaches 100:1 on a weight basis. Substantial oxidation of the SO_2 and H_2S to SO_3 may occur as the hot fumarole gases mix with atmospheric oxygen. The SO_3 then reacts with water vapour to produce sulphuric acid (H_2SO_4) droplets.

The percentages of various sulphur compounds and total sulphur emitted show large variations for different volcanos and also for eruptions from a single volcano. The composition of volcanic gases is roughly 95% H_2O , 4% CO_2 and 1% SO_2 (expressed as

molar percentages). Part of the sulphur emitted by volcanos mixes with air while the remainder precipitates in the vicinity of the eruption.

Although the rate of emission of sulphate compounds from volcanos, averaged over the earth and over time, is probably several orders of magnitude less than that from anthropogenic sources (Kellogg *et al.* 1972), the eruption of a large volcano will have a marked effect on the atmosphere for periods varying from a few days to several weeks. There are no active volcanos in Canada (Geological Survey of Canada 1970), but much of the sulphur emitted outside the country can be carried here.

Hot springs may be a source of H_2S or SO_2 emissions. Waters from springs at Jasper have an unknown free H_2S content (U.S. Geological Survey 1965), while H_2S values of up to 35 mg/L have been reported elsewhere in acidic hot springs. Alkaline hot springs do not contain any free H_2S whereas near-neutral calcareous springs may contain about 2.5 mg/L (Castenholz 1969). No estimates of rates of emission of gaseous sulphur compounds from hot springs are available. Hosler and Kaplan (1966) calculated the amount of global sulphur emitted by hot springs into air and river run-off to be 12 Tg S/yr. It is not known what percentage of this total is released into the air.

A rough estimate of the possible H_2S releases from hot springs was made by assuming that a certain proportion of the aqueous H_2S enters the atmosphere. Observations by Hansen *et al.* (1978) appear to indicate that 0.001% of the H_2S in water is transferred into the air at a temperature of 20°C.

The rate of transport of a substance through a medium by molecular diffusion is directly proportional to its diffusivity. As the temperature increases, the diffusivity of a gas in water also increases. For hot spring temperatures of 80°C to 100°C, the diffusivity is about four to five times greater than at 20°C. Consequently, the movement of H_2S in hot springs to the water-air interface, where it is available for transfer into the atmosphere, is also increased by the same magnitude. This implies that up to 0.01% of the H_2S in hot springs may be released into the air. The H_2S emission rate ($F_{\text{H}_2\text{S}}$) in terms of water flow rates can be expressed as:

$$F_{\text{H}_2\text{S}} = Q \cdot C \cdot K$$

where: Q = hot spring flow rate in L/min
 C = concentration of H_2S in hot springs in mg/L
 K = transfer constant ($\sim 0.01\%$)

Using this relationship for a hot spring with a flow rate of 500 L/min and an H_2S concentration of 2 mg $\text{H}_2\text{S}/\text{L H}_2\text{O}$, the estimated emission rate is 50 g $\text{H}_2\text{S}/\text{yr}$.

There are more than 100 documented hot springs in western Canada with an average flow rate in the vicinity of 500 L/min (U.S. Geological Survey 1965), and a total emission in the order of 5 000 g $\text{H}_2\text{S}/\text{yr}$. Even within several orders of magnitude, these emissions are minor compared with those from other natural sources (accounting for variabilities in flow rates, the number of springs, and release rates).

3.2.3 Soil Dust. An important fraction of atmospheric particulate loadings comes from soils. Even weak winds raise particles of minerals which appear to be a constant component of background loadings. For the most part, the sources are local and confined to arid or semi-arid terrain. The particles settle from the atmosphere or are washed out by rain and then possibly re-entrained into the atmosphere many times over before eventually reaching the ocean (Cadle 1973). Little is known about the rate at which mineral matter, including sulphur compounds, is introduced into the atmosphere.

Lodge *et al.* (1968) suggested that the high concentration of sulphate in precipitation in arid areas of the western, mid-western, and northwestern United States originates from soil dust carried aloft and entrained in river water. The authors noted that calcium carbonate (CaCO_3) and calcium sulphate (CaSO_4) occur in high concentrations in the top soil layer of acid zones. However, the average concentrations tend to vary inversely with the quantity of precipitation, which does not support the hypothesis that increased SO_4 concentrations are a result of wind entrainment of soil dust particles.

Values of sulphate in wet deposition reported by Drozdova *et al.* (1964) were also quite high, in the order of 4 mg S/L, and were accompanied by high calcium concentrations which suggested dusty atmospheric conditions. It is not clear, however, whether this SO_4 originates from gaseous sulphur compounds oxidized to H_2SO_4 , or whether it relates to sulphate soil particles that have become suspended in the air. Granat (1976), reviewing these data, considered windblown dust a contributing source of atmospheric sulphur, at least in or near arid areas.

The production of soil dust is variable in space and time depending on wind speed, precipitation and soil texture. On a regional scale, soil dust may contribute significantly to sulphur concentrations in rainwater (Selezná *et al.* 1967, Lodge 1968).

The global estimate by Granat (1976) was used to obtain a flux estimate for Canada. Granat assumed that one third of the suspended particles from wind erosion are less than 1 μm in diameter and transportable over long distances. He then used the

average sulphur content in weathered rock of 33% cited by Hallberg (1976) and Butcher and Charlson's (1972) global soil dust estimate of 200 Tg/yr, to obtain a global emission of about 0.2×10^6 t S/yr.

Most of the soil sulphur would be from arid and semi-arid regions, which constitute about 42×10^6 km² of the earth's surface (Whittaker 1970). The area of semi-arid and sub-arid land in Canada is about 0.3×10^6 km² (Agriculture Canada 1977). Using the ratio of land surface areas above, a rough estimate of the annual production of sulphur in Canada by wind erosion is $1\,500 \times 10^6$ g S or 0.005 g S/m²/yr in semi-arid and sub-arid areas of Canada. These areas are mainly in the southern Interior Plain of Saskatchewan and Alberta. Some smaller ones are located in the valleys of the British Columbia plateau.

3.2.4 Forest Fires. Forest fires are a possible source of sulphur emissions into the atmosphere as indicated by various researchers. Vines *et al.* (1971) reported detectable SO₂ from Australian bush fires, and Evans and Allen (1971) observed that substantial losses of sulphur occur during the burning of natural vegetation. The amount of gaseous sulphur released is inversely proportional to the amount of basic materials present in combustible tissues and directly proportional to the sulphur content of the combustible materials. If there is sufficient alkalinity, sulphur can be completely retained in a laboratory ashing of plant tissue (Rennie and Halstead 1977). Evans and Allen's studies (1971) and laboratory ashing (Rennie and Halstead 1977) indicated that there is only partial gasification of sulphur from tissue combustion, the remainder staying as ash in the form of basic (non-acidic) sulphur.

Sulphur oxides have been reported to be released from wigwam burners utilizing wood waste (U.S. EPA 1976). From the information available, it appears that sulphur compounds can be released into the atmosphere during forest fires, although the rates have not been accurately determined.

Rennie and Halstead (1977) estimated a forest fire emission of 400 kg SO₂/km² based on a combusted oven-dry wood density of 4 t/ha. They arrived at this factor by considering observations of SO₂ from Australian bush fires (Vines *et al.* 1971), losses of sulphur from the burning of vegetation (Evans and Allen 1971), and an average sulphur content of 0.15% for combusted tissues (Rennie 1972).

Sulphur dioxide emission factors cited for wigwam burners are in the order of 0.05 kg SO₂/t when wood refuse with an approximate moisture content of 50% (U.S. EPA 1976) is burned. Adjusted for oven-dry spruce, which has a bulk density of about 0.4 g/cc,

this factor would be about $0.18 \text{ kg SO}_2/\text{t}$. This corresponds to a forest fire emission of $70 \text{ kg SO}_2/\text{km}^2$, assuming an oven-dry wood density of 4 t/ha .

The above two estimates of sulphur fluxes from forest fires differ substantially. In addition, it has been hypothesized that the nature and amount of gaseous emissions are directly related to variables such as fire intensity and fire direction (relative to the wind), and indirectly related to the rate at which the fire spreads (U.S. EPA 1976). An emission of $200 \text{ kg SO}_2/\text{km}^2$ (100 kg S/km^2), intermediate between 70 and $400 \text{ kg SO}_2/\text{km}^2$, was chosen as an average owing to the lack of more definitive data. This value was applied to data on forest fire occurrence in Canada to estimate annual sulphur emissions (section 4).

4.1 Sulphur Productivity Ranking

The flux of sulphur into the air from natural sources varies over nine orders of magnitude. For soils and coastal areas, Adams (1978c) cited values from $0.001 \text{ g S/m}^2/\text{yr}$ to $2\,000 \text{ g S/m}^2/\text{yr}$. To encompass this wide range, a sulphur productivity ranking based on a logarithmic scale was adopted for this study (Table 10).

TABLE 10 SULPHUR PRODUCTIVITY RANKING

Upper Flux Limit ($\text{g S/m}^2/\text{yr}$)	Rank
10^4	1
10^3	2
10^2	3
10^1	4
10^0	5
10^{-1}	6
10^{-2}	7
10^{-3}	8
10^{-4}	9
10^{-5}	10

Fluxes usually vary with climate, e.g., sulphate reduction by bacteria is temperature dependent. The rank assigned to a specific source represents the sulphur productivity normalized to a base value of the main controlling factor -- in the case of soils, the base emission rate chosen was typical of the growing season. These ranks were subsequently adjusted for different soil climates in Canada before emissions were estimated. The fluxes and ranks by source are identified in sections 4.2 and 4.3.

4.2 Biogenic Sources

4.2.1 Soils. Using the ranking from Table 10, ranks for major soil types were estimated (Table 11) from flux data reported by Adams (1978a, b, c) Hitchcock (1975) and Lovelock (1972):

TABLE 11 SULPHUR PRODUCTIVITY RANKINGS BY SOIL TYPE

Soil Type	Study Ranking		Adams Ranking (1978 a)
	Range	Mean	
Luvisols	6-8	7	6
Brunisols	6-8	7	7
Podzols	7	7	8
Chernozems	6-7	6-7	-
Gleysols	5-6	5-6	4
Organic Terrain	3-9	5-6	2
Alluvial Soils	4-7	6	5
Saline Marshes	2-7	3-6	1

The study ranking appeared to be rather insensitive to differences in soil types compared with the ranking proposed by Adams (1978a). However, Adams's system was subjective and distinguished between fairly similar soil types such as brunisols and podzols.

The soil classifications used in this study were based on those specified by the Soils of Canada (Agriculture Canada 1977). These soil classifications, along with their estimated sulphur productivity rankings, related to the most commonly recorded flux during the growing season, are presented in Table 12.

Since measured fluxes appear to vary by several orders of magnitude with seasonality and location, the study ranking is considered provisional until further field and laboratory studies can be undertaken. The individual ranks presented were adjusted to differences in soil conditions as follows:

1. Soils with higher organic and moisture contents have been ranked slightly higher;
2. Soils seasonally or continuously waterlogged have been ranked higher;
3. Soils with low porosity and aerobic horizons have been ranked slightly lower;
4. Acidic soils such as some fibrosols are ranked lower, since organisms producing volatile sulphur compounds grow more slowly below pH 5.5.

TABLE 12 SOIL CLASSIFICATIONS AND THEIR SULPHUR PRODUCTIVITY RANKINGS

Classification		Rank
A Chernozemic	A1 Brown	7
	A2 Dark Brown	6
	A3 Black	6
	A4 Dark Gray	7
B Solonetzic	B1 B2 Solonetz	6
	B4 Solod	6
C Luvisolic	C1 Gray Brown Luvisol	7
	C2 Gray Luvisol	7
D Podzolic	D1 Humic Podzol	6
	D2 Ferro-Humic Podzol	7
	D3 Humo-Ferric Podzol	7
E Brunisolic	E1 Melanic Brunisol	7
	E2 Eutric Brunisol	7
	E2 Sombric Brunisol	7
	E3 Dystric Brunisol	6
F Regosolic	F Regosolic	7
G Gleysolic	G1 Humic Gleysol	5
	G2 Gleysol	6
	G3 Eluviated Gleysol	6
H Organic	H1 Fibrisol	6
	H2 Mesisol	3-5
	H3 Humisol	3-5
R Rockland		8

Corrections to the rankings are required for different mean temperature and soil climate conditions in Canada. Organisms involved in H_2S and other volatile organic sulphur production (Adams 1978a, b and c) are sensitive to temperature, with extremely low production rates below 10°C. Adams (*loc.cit.*) has identified a tenfold increase in activity between 15°C and 20°C and between 20°C and 30°C. Using these data, soil ranking adjustments according to soil climate were formulated as follows:

Reduction of 1 to 2

Arctic and sub-arctic
soil climates

Reduction of 1

Cryoboreal soil climates

No reduction or less than 1

Boreal soil climates

Rank remains unchanged

Mesic soil climates

A preliminary estimate of sulphur emissions from soils in Canada was made from soil land area data and derived sulphur productivity rankings (Table 13).

TABLE 13 EMISSIONS OF VOLATILE SULPHUR FROM CANADIAN SOILS

	Area ₃ (x 10 ³ km)	Rank*	Maximum Sulphur Emissions t/yr
A Chernozemic			
Brown	100.6	7	1 010
Dark Brown	111.1	6	11 110
Black	200.7	6	20 070
Dark Gray	56.2	7	560
			32 750
B Solonetzic	72.6	6	7 260
C Luvisolic	809.3	7	8 090
D Podzolic	2 072.9	7	20 730
E Brunisolic			
Melanic	27.7	8	30
Eutric	556.7	7	5 570
Dystric	382.2	6	38 220
			43 820
F Regosolic	2 277.4	7	22 770
G Gleysolic	213.2	5-6	106 600
H Organic	927.4	6	92 740
Total			334 760

* Temperature correction was not applied for northern soil climates.

The total emissions of volatile sulphur from Canadian soils, estimated in Table 13, may reach 0.33 Tg S/yr. This is likely an overestimate because a significant proportion of regosolic, gleysolic and organic soils are within northern soil climate regions (Alberta, Ontario) where sulphur production is likely much lower. Temperature corrections were applied to the revised detailed estimate of sulphur emissions from soils on a county basis and are tabulated in section 5.

4.2.2 Vegetation. Lovelock *et al.* (1972) demonstrated that leaves of trees and herbs produced DMS in significant amounts, which increased considerably during senescence. The annual primary production in terrestrial areas decreases northward with shorter growing seasons and lower temperatures. Productivity studies such as those by Westlake (1963) indicate that coniferous forests, deciduous forests and terrestrial herbs assimilate approximately 28, 12 and 20 t/ha/yr respectively. Approximately 50% of these standing crops would be above ground.

DMS fluxes from leaves, presented in Table 14, were estimated from data from Lovelock *et al.* (1972) and the standing crop data of Westlake (1963).

TABLE 14 DMS FLUXES FOR VEGETATION

Type of Vegetation	Standing Crop (g/m ²)	DMS Production (g/m ² /h)	DMS Flux (10 ⁻⁶ g/m ² /yr for 180 days)
Coniferous forest	14 x 10 ²	28 - 602 x 10 ⁻¹⁰	10.4 - 263.0
Deciduous forest	6 x 10 ²	12 - 258 x 10 ⁻¹⁰	5.2 - 112.7
Terrestrial forest	10 x 10 ²	20 - 430 x 10 ⁻¹⁰	8.7 - 188.0

The figures in Table 14 suggest vegetation ranks between 8 and 10, several orders of magnitude lower than those determined for soils. During senescence, DMS evolution could be two to three times higher than that observed during the remainder of the year. Release of other volatile sulphur compounds by vegetation could also contribute to atmospheric loadings.

The ranks assigned to sulphur production from the three vegetation groups, based on the estimates presented in Table 14 and adjusted for increased production during senescence, are as follows:

	Rank	Mean Rank
Coniferous forest	9 - 7	8
Deciduous forest	9 - 7	8
Terrestrial herbs	10 - 8	9

Since standing crops from arctic, sub-arctic and cryoboreal regions are lower (Westlake 1963, Pearsall and Gorham 1956), soil ranking adjustments were made as follows:

Reduction of 2	Arctic soil climates
Reduction of 1	Sub-arctic soil climates
Reduction of zero to 1	Cryoboreal soil climates

Consideration of these soil climate ranking adjustments results in the sulphur productivity ranking shown in Table 15.

TABLE 15 SULPHUR PRODUCTIVITY RANKING FOR VARIOUS VEGETATION SOURCES AND SOIL CLIMATES

Vegetation	Soil Climate	Study Ranking
Tundra	arctic	10
Tundra	sub-arctic	9
Coniferous and mixed forests	boreal	7-8
Deciduous forest	mesic	7-8

These rankings were applied to measured land areas by vegetation types for Canada to obtain an annual emission rate. The results of this estimate are given in section 5.

An alternative method for assessing the role of vegetation in sulphur production is presented in section 5. Provincial estimates of sulphur emissions for typical vegetation in each of the soil temperature climates indicate that boreal forest environments are important vegetational sulphur sources (see Table 35).

4.2.3 Aquatic Systems. Volatile sulphur emissions from aquatic systems occur primarily from shoreline and littoral regions. The primary component appears to be H_2S (Jorgensen and Cohen, 1977; Hansen et al. 1978), which is produced in anaerobic muds and must diffuse through the water column before entering the atmosphere.

Several researchers have shown that, because of the short life of H_2S in aerobic water, emissions would be confined to lake margins. Hydrogen sulphide produced in deeper sediments would be oxidized to SO_4 in the water column and could, in poorly

buffered lakes, contribute significantly to the development of acidic hypolimnetic waters. Some volatile organic sulphur compounds such as DMS and DMDS are known to be emitted from various algae and also from the surface of lake or ocean water. However, the amount measured is generally small.

The freshwater biogenic classification has been based essentially on the trophic status of the freshwater lakes, which may be categorized, according to the amounts of nutrients they receive, into eutrophic, mesotrophic and oligotrophic systems.

Eutrophic lakes frequently develop anaerobic hypolimnetic conditions, a potential atmospheric sulphur source during the fall overturn. As well, these lakes may have nutrient-rich muds in littoral and sublittoral regions.

Mesotrophic and oligotrophic lakes are poorer in nutrients and tend to be deeper. Marginal areas, such as the littoral zone, tend to be more restricted in representation. Potential sulphur productivity from such lakes may differ by more than an order of magnitude.

Lakes in northern regions of Canada often tend to be dystrophic, and have low overall productivity because of the acidic conditions, abundance of peat colloids, and low light penetration.

Following the ranking system from Table 10, a ranking for the major lake types was determined from the concentration and flux data reported by Jorgensen and Cohen (1977), Hansen *et al.* (1978) and others. It is shown in Table 16.

TABLE 16 FRESHWATER BIOGENIC CLASSIFICATIONS AND SULPHUR PRODUCTIVITY RANKING

Biogenic Classification	Rank
Rock Shorelines	10
Littoral Muds (exposed)	3-6
Swamps and Marsh Shorelines	3-5
Eutrophic Lakes	6
Mesotrophic Lakes	7
Oligotrophic Lakes	8
Dystrophic and Bog Lakes	9

Total emissions of volatile sulphur from freshwater lakes, on a provincial basis, are tabulated in section 5. The Canadian total is estimated at 11 898 t/yr.

Coastal areas have been classified according to Owens (1977) and rankings established on the basis of the shoreline characteristics within each of the marine divisions (Table 17). Total coastal sulphur emissions for each of the marine divisions are tabulated in section 5.

TABLE 17 MARINE BIOGENIC CLASSIFICATIONS AND SULPHUR PRODUCTIVITY RANKING

I	<u>Rock or Cliff Shores</u>	Rank
	(1) exposed resistant coast with low backshore or cliffs	10
	(2) sheltered resistant coasts	10
	(3) exposed unresistant cliffs	10
	(4) sheltered unresistant cliffs	10
II	<u>Shorelines with Beaches</u>	
	(5) cobble or mixed sediment beaches	7
	(6) sand beaches	5
	(7) pocket beaches	4
	(8) sheltered beaches (lagoons)	3-4
III	<u>Shorelines with Intertidal Sediments</u>	
	(9) coarse sediments on a wave-cut platform	4
	(10) intertidal mud	3-4
	(11) intertidal sand	3-4
IV	<u>Shorelines with Vegetation</u>	
	(12) marshes and swamps	2-4

Temperature corrections have been made for freshwater and coastal sources, using mean annual temperatures and the soil temperature classes following those outlined for soils and vegetation.

4.3 Other Sources

4.3.1 Sea and Lake Spray. Sea-salt-sulphate fluxes, as a function of wind speed, were estimated using derived sea-salt production rates (Toba 1965) and scaling by the weight of SO_4 contained in a sea-salt particle. The estimated fluxes, as a function of wind speed, are as follows:

SO_4 Fluxes (g S/m ² /yr)	Wind Speed (km/h)
0.06	11
0.08	14
0.14	18
0.22	22

The annual mean wind speed in coastal areas in Canada usually ranges from 10 to 15 km/h (Canada Department of Transport 1968), so that an average sea-salt-sulphate flux of 0.07 g S/m²/yr was selected. This corresponds to a sulphur productivity ranking of 6.

The sea-salt fluxes, on an annual basis, for Canadian coastal areas were calculated by summing the individual seasonal contributions. Where ice formed, it was assumed that no sea-salt-sulphate was produced in the area. The annual fluxes derived for the major coastal areas in Canada are listed in Table 18.

$$\text{Emission Rate} = \text{Ice-free Period Fraction} \times \text{Area (m}^2\text{)} \times \text{Sulphate Flux}$$

Lake sulphate production by the sea-spray mechanism was calculated by scaling the sea-sulphate flux by the ratio of SO_4 concentration in lake water to that in seawater. An average lake water SO_4 concentration of 4 mg SO_4 /L was used to calculate the base rate (i.e., the average seawater sulphate concentration is 2.5 g SO_4 /L). Sulphate fluxes as a function of wind speed are listed below:

SO_4 Flux (g S/m ² /yr)	Wind Speed (km/h)
0.0001	11
0.0001	14
0.0002	18
0.0004	22

These flux estimates for lake sulphate sources are in the order of 10^3 times smaller than sea-salt fluxes. A sulphate flux of 7×10^{-5} g S/m²/yr was adopted, which corresponds to a sulphur productivity rank of 9. This rate was applied to lakes of 1 000 km² or more in area, based on the assumption that these lakes would have a sufficient fetch to produce substantial waves (section 5). The estimated lake emissions

TABLE 18 SEA-SALT FLUXES FOR COASTAL AREAS

	Wind Speed (km/h)	Sulphate Fluxes (g S/m ² /season)
Pacific Ocean		
Dec.-Feb.	17*	0.03
Mar.-May	13	0.02
June-Aug.	10	0.01
Sept.-Nov.	12	0.01
Annual		0.07
Atlantic Ocean		
Dec.-Feb.	23	0.06
Mar.-May	21	0.06
June-Aug.	15	0.02
Sept.-Nov.	19	0.03
Annual		0.17
Labrador Sea		
Dec.-Feb.	ice**	-
Mar.-May	ice	-
June-Aug.	14	0.02
Sept.-Nov.	16	0.02
Annual		0.04
Hudson Bay		
Dec.-Feb.	ice	-
Mar.-May	ice	-
June-Aug.	21 (1/2 ice)	0.03
Sept.-Nov.	27 (1/2 ice)	0.04
Annual		0.07
Beaufort Sea		
Dec.-Feb.	ice	-
Mar.-May	ice	-
June-Aug.	21	0.06
Sept.-Nov.	ice	-
Annual		0.06

* wind data from Canada Department of Transport (1968)

** ice data from Atmospheric Environment Service (1972)

were multiplied by the ice-free period (no production of sulphate would occur with ice cover) to obtain the annual emission.

4.3.2 Soil Dust. A sulphur flux was derived for wind-suspended soil particles from semi-arid and sub-arid land in Canada from the global estimate of Granat (1976). The flux for Canada was $0.0005 \text{ g S/m}^2/\text{yr}$, which corresponds to a sulphur productivity rank of 8. The variability of this estimate is likely greater than an order of magnitude.

4.3.3 Forest Fires. Forest fires may release SO_2 at a rate of about $1 \times 10^5 \text{ g S}$ for each square kilometre burned. In Canada an average of about $10\,200 \text{ km}^2$ are burned annually, yielding $10^{-5} \text{ g S/m}^2/\text{yr}$. This corresponds to a sulphur productivity rank of 10. The annual sulphur emissions by province are listed in Table 19.

TABLE 19 ESTIMATED ANNUAL SULPHUR EMISSIONS FROM FOREST FIRES, CANADA

Province/Territory	Emissions (10^6 g S)
Newfoundland	81
Prince Edward Island	-
Nova Scotia	3
New Brunswick	5
Quebec	60
Ontario	55
Manitoba	203
Saskatchewan	164
Alberta	64
British Columbia	171
Yukon and Northwest Territories	194
Canada	1 000

The sulphur emissions in any year will vary greatly depending on the number of forest fires. Values for the 1971-76 period were calculated for Ontario and are listed in Table 20.

TABLE 20 ESTIMATED SULPHUR EMISSIONS FROM FOREST FIRES IN ONTARIO, 1971-76

Year	Area Burned (km ²)	Emissions (10 ⁶ g S)
1976	5 470	547
1975	169	17
1974	5 267	527
1973	36	4
1972	322	32
1971	147	15

In severe years, Ontario alone can contribute over half the average sulphur emissions expected for Canada.

4.3.4 Miscellaneous. Hot springs are considered potential sources of H₂S. The release was estimated to be about 5 000 g H₂S/yr for hot springs located in British Columbia and Alberta. Volcanos are large-point sources of SO₂ but there are no active ones in Canada. However, the gases and particles emitted from volcanos in other countries are transported over large distances and contribute to the natural atmospheric sulphur budget for Canada. Because of lack of data, no estimate of this contribution has been made.

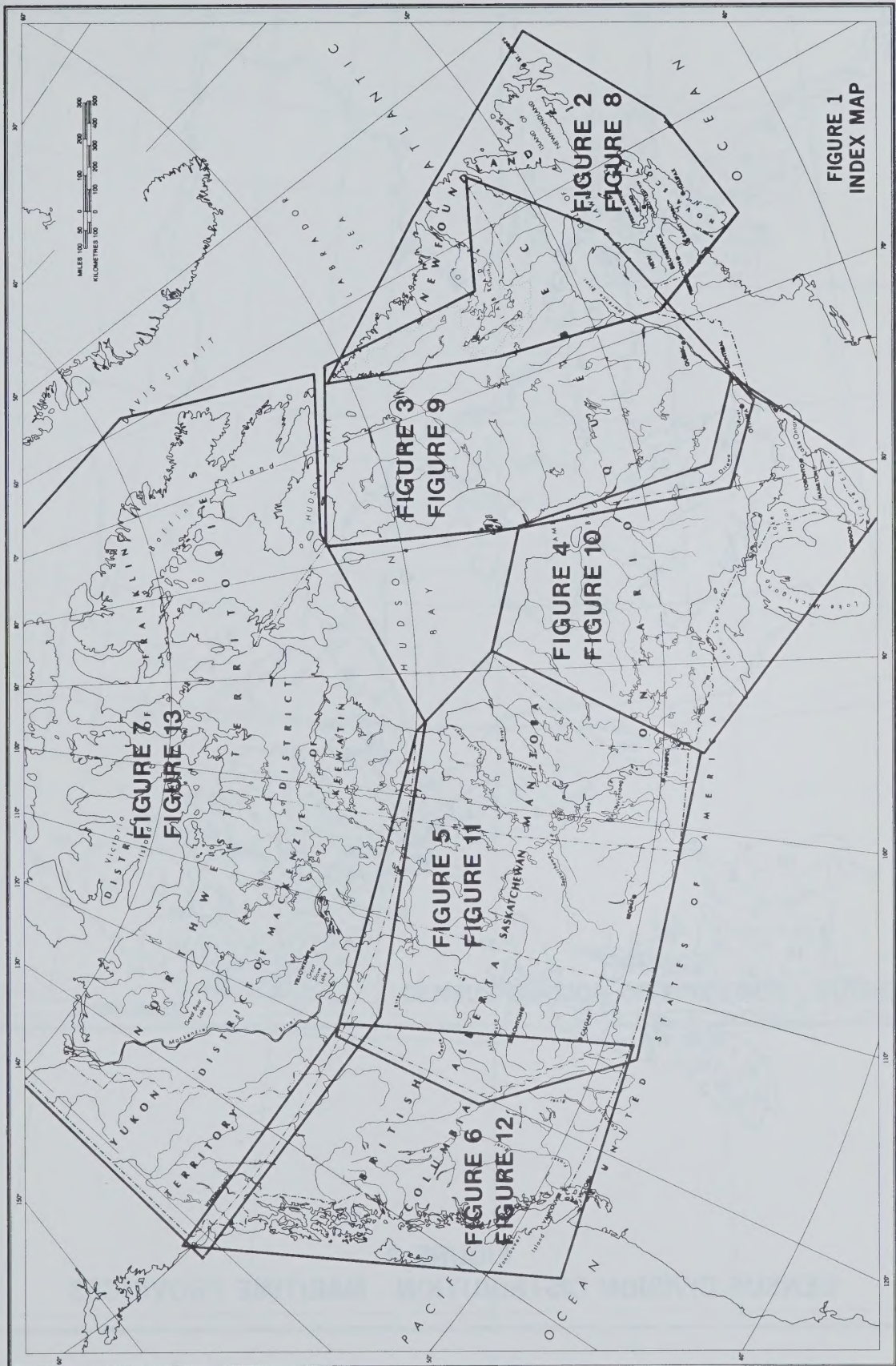
5 ANNUAL NATURAL EMISSIONS OF SULPHUR IN CANADA

5.1 Biogenic Emissions

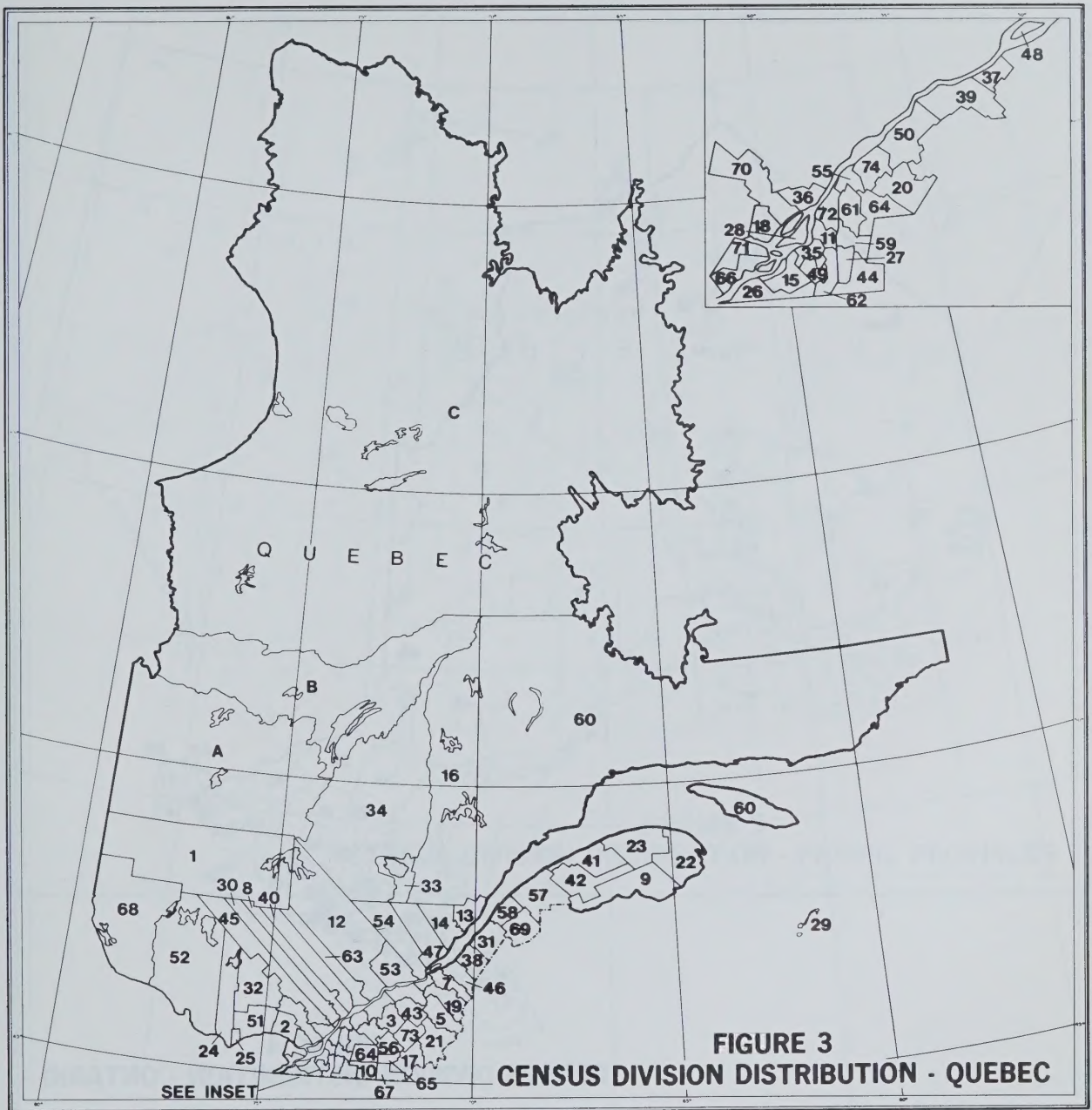
This section presents the estimates of biogenic emissions from land and marine areas. Figure 1 is an index to census division maps (Figures 2-7) and corresponding soil and marine classification maps (Figures 8-13). The latter maps also illustrate high (rank 5) and moderate (rank 6-7) sulphur productivity from marine and census divisions. Figures 8-13 are appended to this report.

5.1.1 Soils. Tables of emission estimates are provided for soils (Tables 21-33). Table 21 is a provincial summary of sulphur emissions from soils as obtained from the detailed census division estimates in Tables 22-33. The latter provide quantitative information on the land area of various soil types by census division for Canada. The locations of these divisions are identified in Figures 2 to 7.

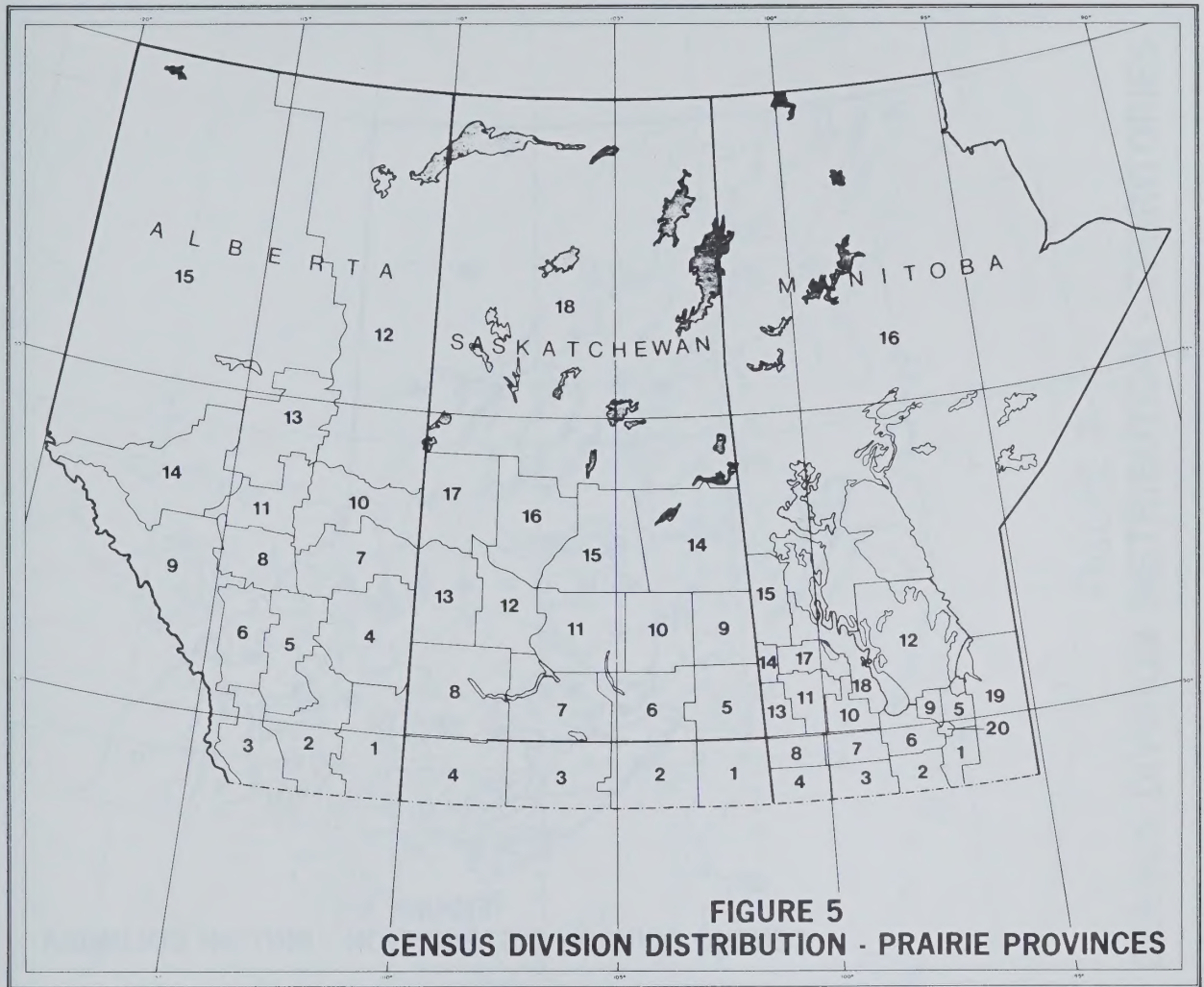
Each soil type was evaluated according to soil rankings shown in Table 12. A census division rank was derived from the logarithmic average of soil type land area, weighted by its respective rank. The census division rank was then used to determine the sulphur emissions for the division.











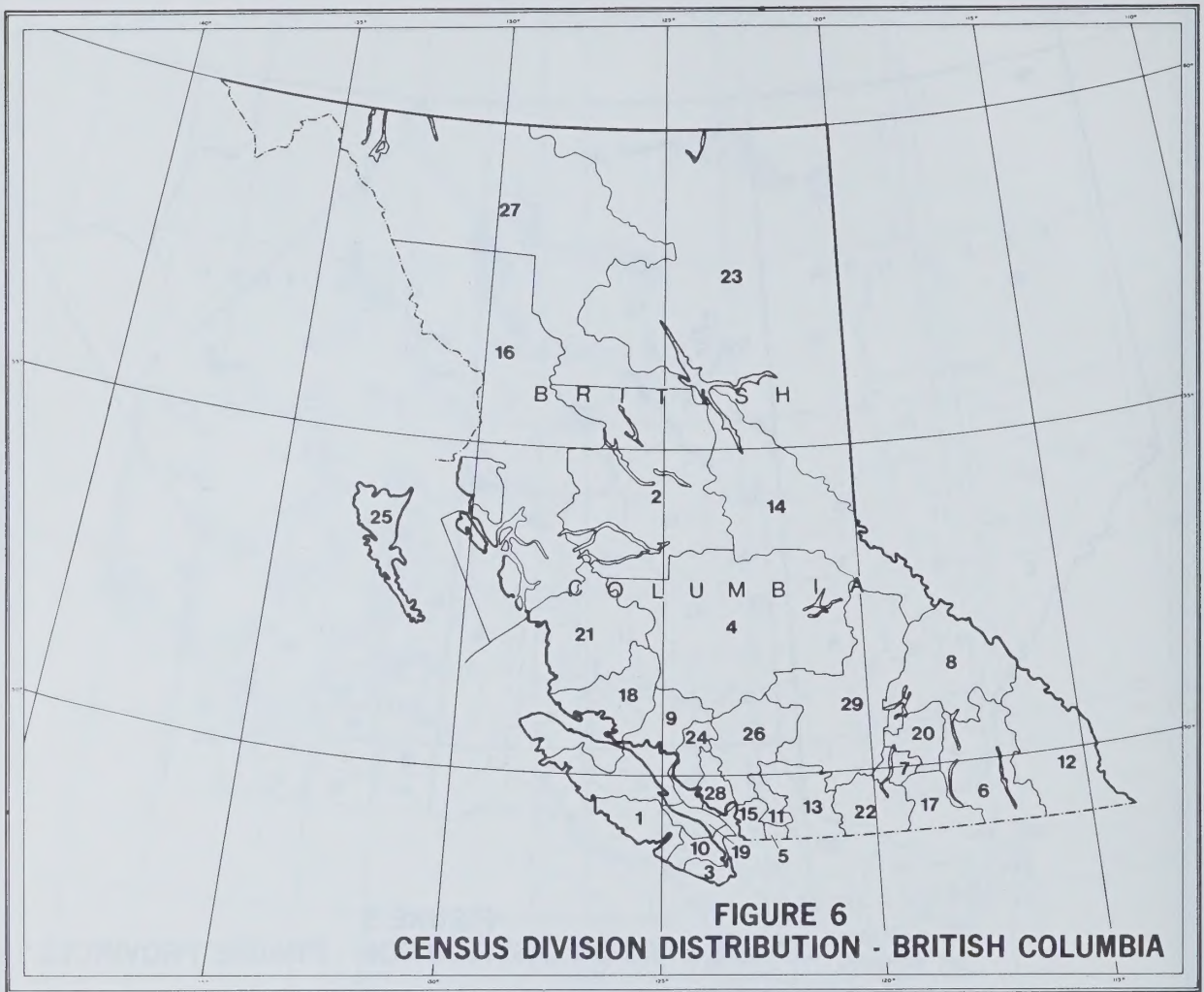




TABLE 21 ANNUAL EMISSIONS OF SULPHUR FROM SOILS, CANADA, BY
PROVINCE/TERRITORY

Province	Annual Emissions (t as S)
Newfoundland	2 187
Prince Edward Island	72
Nova Scotia	609
New Brunswick	761
Quebec	23 888
Ontario	65 672
Manitoba	47 860
Saskatchewan	17 217
Alberta	31 062
British Columbia	29 515
Yukon Territory	4 950
Northwest Territories	22 770
Canada Total	246 563

TABLE 22 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, NEWFOUNDLAND

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	--	podzolic	9 055	7	7	9.06
2	--	podzolic	6 305	7	7	6.31
3	--	podzolic	21 066	7	7	21.07
4	--	podzolic	5 455	7		
		luvisolic	1 843	7		
					7	7.39
5	--	podzolic	9 139	7	7	9.14
6	--	podzolic	18 130	7	7	18.13
7	--	podzolic	9 943	7	7	9.94
8	--	podzolic	9 539	7	7	9.54
9	--	podzolic	14 410	7	7	14.41
10	--	podzolic	61 897	7		
		organic	8 702	6		
		rockland	156 871	8		
					7-8	113.74
Total						218.73

TABLE 23 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, PRINCE EDWARD ISLAND

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	Kings	podzolic	2 253	7	7	2.25
2	Prince	podzolic	2 354	7	7	2.35
3	Queens	podzolic	2 560	7	7	2.56
Total						7.16

TABLE 24 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, NOVA SCOTIA

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	Annapolis	podzolic	4 094	7	7	4.09
2	Antigonish	luvisolic	922	7		
		podzolic	819	7	7	1.74
3	Cape Breton	podzolic	2 874	7	7	2.87
4	Colchester	luvisolic	1 536	7		
		podzolic	2 355	7	7	3.89
5	Cumberland	luvisolic	1 536	7		
		podzolic	2 559	7		
		regosolic	409	8	7	4.50
6	Digby	podzolic	3 071	7	7	3.07
7	Guysborough	luvisolic	205	7		
		podzolic	4 505	7	7	4.71
8	Halifax	luvisolic	4 198	7		
		podzolic	1 330	7	7	5.53
9	Hants	luvisolic	1 741	7		
		podzolic	1 638	7	7	3.38
10	Inverness	luvisolic	1 741	7		
		podzolic	2 355	7	7	4.10
11	Kings	luvisolic	102	7		
		podzolic	2 253	7	7	2.35
12	Lunenburg	podzolic	3 481	7	7	3.48
13	Pictou	luvisolic	1 126	7		
		podzolic	2 150	7	7	3.28
14	Queens	podzolic	3 174	7	7	3.17

TABLE 24 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, NOVA SCOTIA (continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
15	Richmond	luvisolic podzolic	1 024 511	7 7	7	1.53
16	Shelborne	podzolic	2 867	7	7	2.87
17	Victoria	podzolic	2 969	7	7	2.97
18	Yarmouth	podzolic	3 379	7	7	3.38
Total						60.91

TABLE 25 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, NEW BRUNSWICK

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	Albert	luvisolic podzolic	409 1 638	7 7	7	2.04
2	Carleton	podzolic	3 584	7	7	3.58
3	Charlotte	podzolic	3 585	7	7	3.58
4	Gloucester	luvisolic podzolic	2 150 2 662	7 7	7	4.81
5	Kent	luvisolic podzolic	3 686 1 229	7 7	7	4.91
6	Kings	luvisolic podzolic	819 2 458	7 7	7	3.27
7	Madawaska	podzolic	3 276	7	7	3.28
8	Northumberland	luvisolic podzolic	5 018 7 372	7 7	7	12.39
9	Queens	luvisolic podzolic	1 946 1 434	7 7	7	3.18
10	Restigouche	podzolic	9 010	7	7	9.01
11	St. John	podzolic	1 638	7	7	1.64
12	Sunbury	luvisolic podzolic	1 536 1 126	7 7	7	2.66
13	Victoria	podzolic	6 450	7	7	6.45
14	Westmorland	luvisolic podzolic regosolic	2 253 2 765 205	7 7 7	7	5.22
15	York	luvisolic podzolic	1 741 8 294	7 7	7	10.03
Total						76.05

TABLE 26 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, QUEBEC

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	Abitibi	luvisolic podzolic	10 342 30 205	7 7	7	40.54
2	Argenteuil	brunisolic gleysolic	1 741 205	6-7 5-6	6	19.46
3	Arthabaska	podzolic	1 740	7	7	1.74
4	Bagot	podzolic brunisolic	715 306	7 6-7	7	1.02
5	Beauce	podzolic	2 665	7	7	2.67
6	Beauharnois	brunisolic	205	6-7	6-7	1.03
7	Bellechasse	podzolic	2 457	7	7	2.46
8	Berthier	podzolic gleysolic	7 373 410	7 5-6	6	7.78
9	Bonaventure	podzolic brunisolic	512 2 367	7 6-7	6-7	14.40
10	Brome	podzolic	3 072	7	7	3.07
11	Chambly	podzolic brunisolic gleysolic	2 048 52 51	7 6-7 5-6	6-7	10.75
12	Champlain	podzolic	23 653	7	7	23.65
13	Charlevoix-Est	podzolic rockland	2 048 510	7 8	7	2.56
14	Charlevoix-Ouest	podzolic rockland	2 030 1 945	7 8	7	3.98
15	Châteauguay	brunisolic gleysolic	520 104	6-7 5-6	6	6.24

TABLE 26 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, QUEBEC
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
16	Chicoutimi	podzolic rockland	33 995 5 222	7 8	7	39.22
17	Compton	podzolic	2 048	7	7	2.05
18	Deux-Montagnes	brunisollic	819	6-7	6-7	4.10
19	Dorchester	podzolic	2 457	7	7	2.56
20	Drummond	podzolic	1 434	7	7	1.43
21	Frontenac	podzolic	3 379	7	7	3.38
22	Gaspé-Est	podzolic brunisollic	2 560 4 403	7 6-7	6-7	34.82
23	Gaspé-Ouest	podzolic	5 939	7	7	5.94
24	Gatineau	podzolic brunisollic gleysolic	1 331 1 024 3 175	7 6-7 5-6	5-6	276.50
25	Hull	gleysolic	409	5-6	5-6	20.50
26	Huntingdon	podzolic gleysolic	405 614	7 5-6	5-6	50.90
27	Iberville	brunisollic	512	6-7	6-7	2.56
28	Île-de-Montréal et Île-Jésus	brunisollic	307	6-7	6-7	1.55
29	Îles-de-la- Madeleine	brunisollic	200	6-7	6-7	1.00
30	Joliette	podzolic gleysolic brunisollic	6 143 306 205	7 5-6 6-7	6	66.50
31	Kamouraska	podzolic	2 969	7	7	2.97
32	Labelle	podzolic brunisollic gleysolic	5 765 3 482 717	7 6-7 5-6	6	99.64

TABLE 26 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, QUEBEC
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
33	Lac St. Jean - Est	podzolic gleysolic	2 252 922	7 5-6	6	31.74
34	Lac St. Jean - Ouest	podzolic gleysolic rockland	54 577 717 2 253	7 5-6 8	7	57.55
35	Laprairie	gleysolic	409	5-6	5-6	20.45
36	L'Assomption	podzolic brunisolic	307 410	7 6-7	6-7	3.59
37	Lévis	podzolic	409	7	7	0.41
38	L'Islet	podzolic	2 252	7	7	2.25
39	Lotbinière	podzolic	1 843	7	7	1.84
40	Maskinongé	podzolic gleysolic	5 836 307	7 5-6	6-7	30.70
41	Matane	podzolic	4 607	7	7	4.61
42	Matapédia	podzolic	3 582	7	7	3.58
43	Mégantic	podzolic	1 945	7	7	1.95
44	Missisquoi	podzolic luvisolic brunisolic	102 103 818	7 7 6-7	6-7	5.12
45	Montcalm	podzolic brunisolic gleysolic	5 409 1 024 512	7 6-7 5-6	6	69.40
46	Montmagny	podzolic	1 739	7	7	1.74
47	Montmorency 1	podzolic rockland	3 891 1 741	7 8	7	5.63
48	Montmorency 2	podzolic	189	7	7	0.19
49	Napierville	brunisolic gleysolic	102 205	6-7 5-6	5-6	15.35

TABLE 26 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, QUEBEC
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
50	Nicolet	podzolic	1 433	7	7	1.43
51	Papineau	brunisollic gleysolic	2 253 1 843	6-7 5-6	5-6	204.80
52	Pontiac	brunisollic gleysolic podzolic	3 354 2 236 19 620	6-7 5-6 7	6-7	126.10
53	Portneuf	podzolic	4 095	7	7	4.10
54	Québec	podzolic rockland	6 040 819	7 8	7	6.86
55	Richelieu	podzolic gleysolic	358 51	7 5-6	6-7	2.05
56	Richmond	podzolic	1 433	7	7	1.43
57	Rimouski	podzolic	5 734	7	7	5.73
58	Rivière-du-Loup	podzolic	3 481	7	7	3.48
59	Rouville	brunisollic gleysolic	409 204	6-7 5-6	6	6.14
60	Saguenay	brunisollic podzolic rockland	4 914 187 698 20 462	6-7 7 8	7	213.07
61	St. Hyacinthe	podzolic brunisollic gleysolic	102 205 409	7 6-7 5-6	5-6	35.80
62	St. Jean	brunisollic	409	6-7	6-7	2.05
63	St. Maurice	podzolic	4 709 307	7 5-6	6-7	25.10
64	Shefford	podzolic brunisollic	1 228 308	7 6-7	7	1.53

TABLE 26 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, QUEBEC
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
65	Sherbrooke	brunisollic gleysolic	614 103	6-7 5-6		
					6-7	3.56
66	Soulanges	gleysolic	346	5-6	5-6	17.30
67	Stanstead	podzolic	1 228	7	7	1.23
68	Témiscamingue	podzolic luvisolic	22 654 1 530	7 7		
					7	24.18
69	Témiscouata	podzolic	1 941	7	7	1.94
70	Terrebonne	podzolic brunisollic	409 2 047	7 6-7		
					6-7	12.28
71	Vaudreuil	brunisollic	511	6-7	6-7	2.56
72	Verchères	podzolic gleysolic	307 205	7 5-6		
					6	5.12
73	Wolfe	podzolic	920	7	7	0.92
74	Yamaska	podzolic	921	7	7	0.92
A	Abitibi	podzolic luvisolic organic	39 320 1 617 10 940	7 7 6		
					6-7	259.40
B	Mistassini	podzolic organic rockland	56 519 17 516 409	7 6 8		
					6-7	372.20
C	Nouveau-Québec	podzolic organic rockland	156 669 50 073 511 276	8 7 9		
					8-9	35.90
Total						2 388.80

TABLE 27 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, ONTARIO

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	Algoma	podzolic brunisollic rockland	50 586 2 969 307	7 6-7 8	7	53.86
2	Brant	brunisollic	9 369	6-7	6-7	46.90
3	Bruce	podzolic brunisollic	1 843 2 815	7 6-7	6-7	23.30
4	Cochrane	luvisollic podzolic gleysollic organic	16 891 23 039 29 490 73 931	7 7 5-6 6	6	1 433.00
5	Dufferin	luvisollic brunisollic	1 380 92	7 7	7	1.47
6	Dundas	podzolic brunisollic gleysollic	51 205 614	7 6-7 5-6	5-6	43.50
7	Durham	luvisollic	1 639	7	7	1.64
8	Elgin	luvisollic gleysollic	2 355 51	7 5-6	7	2.41
9	Essex	luvisollic	205	7	7	0.21
10	Frontenac	luvisollic podzolic brunisollic	717 309 1 639	7 7 6-7	6-7	13.30
11	Glengarry	brunisollic gleysollic	870 205	6-7 5-6	5-6	54.00
12	Grenville	brunisollic gleysollic	259 409	6-7 5-6	5-6	33.40
13	Grey	podzolic brunisollic	2 967 2 046	7 6-7	7	5.01

TABLE 27 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, ONTARIO
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
14	Haldimand	luvisolic	1 230	7	7	1.23
15	Haliburton	podzolic	4 710	7	7	4.71
16	Halton	luvisolic	921	7	7	0.92
17	Hastings	luvisolic	820	7		
		podzolic	4 403	7		
		brunisollic	1 229	6-7		
					7	6.45
18	Huron	gleysolic	864	5-6		
		luvisolic	2 500	7		
					6	33.64
19	Kenora	luvisolic	41 881	7		
		podzolic	144 076	7		
		gleysolic	29 081	5-6		
		organic	169 983	6		
		rockland	11 674	8		
					6	3 967.50
20	Kent	luvisolic	1 024	7		
		gleysolic	1 741	5-6		
					5-6	138.00
21	Lambton	luvisolic	819	7		
		gleysolic	2 048	5-6		
					5-6	143.00
22	Lanark	luvisolic	205	7		
		podzolic	1 024	7		
		brunisollic	1 945	6-7		
					7	3.20
23	Leeds	luvisolic	614	7		
		podzolic	803	7		
		brunisollic	920	6-7		
					7	2.32
24	Lennox and Addington	luvisolic	614	7		
		podzolic	819	7		
		brunisollic	912	6-7		
					7	2.40
25	Manitoulin	brunisollic	4 505	6-7	6-7	22.60

TABLE 27 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, ONTARIO
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
26	Middlesex	luvisolic gleysolic	3 276 102	7 5-6	7	3.38
27	Muskoka	podzolic	4 300	7	7	4.30
28	Niagara	luvisolic gleysolic	1 228 819	7 5-6	6	20.47
29	Nipissing	podzolic gleysolic	18 022 614	7 5-6	6-7	93.20
30	Norfolk	luvisolic	1 944	7	7	1.94
31	Northumberland	luvisolic	1 945	7	7	1.94
32	Ontario	podzolic luvisolic	102 1 945	7 7	7	2.05
33	Ottawa - Carleton	brunisollic luvisolic gleysolic	2 149 1 331 204	6-7 7 5-6	6-7	18.35
34	Oxford	luvisolic	2 047	7	7	2.05
35	Parry Sound	rockland podzolic	1 228 9 011	8 7	7	10.23
36	Peel	luvisolic	1 279	7	7	1.28
37	Perth	gleysolic luvisolic	542 1 624	5-6 7	6	21.66
38	Peterborough	podzolic brunisollic luvisolic	2 048 306 1 433	7 6-7 7	7	3.78
39	Prescott	podzolic brunisollic	102 204	7 6-7	7	0.30
40	Prince Edward	brunisollic	1 228	6-7	6-7	6.15

TABLE 27 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, ONTARIO
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
41	Rainy River	luvisolic podzolic	3 481 15 461	7 7	7	18.94
42	Renfrew	podzolic	512	7	7	0.51
43	Russell	podzolic brunisollic	409 102	7 6-7	7	0.51
44	Simcoe	luvisolic podzolic brunisollic	2 968 521 204	7 7 6-7	7	3.72
45	Stormont	podzolic brunisollic gleysolic	51 512 204	7 6-7 5-6	6	7.67
46	Sudbury	podzolic brunisollic gleysolic rockland	39 936 4 915 1 331 1 228	7 6-7 5-6 8	6-7	236.90
47	Thunder Bay	luvisolic podzolic brunisollic rockland	6 040 102 806 819 1 945	7 7 6-7 8	7	111.60
48	Timiskaming	luvisolic podzolic	2 457 14 028	7 7	7	16.48
49	Toronto	luvisolic	620	7	7	0.62
50	Victoria	luvisolic brunisollic	2 251 819	7 6-7	7	3.07
51	Waterloo	luvisolic	1 313	7	7	1.31
52	Wellington	luvisolic	2 627	7	7	2.63

TABLE 27 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, ONTARIO
(continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
53	Wentworth	luvisolic	1 177	7	7	1.18
54	York	luvisolic	1 735	7	7	1.74
Total						6 567.20

TABLE 28 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, MANITOBA

Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	chernozemic	2 559	6-7		
	luvisolic	409	7		
	regosolic	307	7		
	gleysolic	716	5-6		
	organic	204	6		
				6	41.90
2	chernozemic	4 709	6-7		
	gleysolic	921	5-6		
				6	56.30
3	chernozemic	6 449	6-7	6-7	32.30
4	chernozemic	6 143	6-7	6-7	30.70
5	chernozemic	1 145	6-7		
	luvisolic	307	7		
				6-7	7.40
6	chernozemic	6 347	6-7	6-7	31.80
7	chernozemic	5 731	6-7	6-7	28.65
8	chernozemic	5 323	6-7	6-7	26.60
9	chernozemic	3 071	6-7	6-7	15.35
10	chernozemic	4 402	6-7		
	luvisolic	716	7		
				6-7	25.60
11	chernozemic	3 276	6-7		
	luvisolic	3 993	7		
				7	7.30
12	chernozemic	11 058	7		
	luvisolic	11 161	6-7		
				7	22.20
13	chernozemic	4 812	6-7		
	luvisolic	102	7		
				6-7	24.60
14	chernozemic	1 125	6-7		
	luvisolic	920	7		
				6-7	10.30
15	chernozemic	3 685	6-7		
	luvisolic	4 670	7		
	organic	716	7		
				7	9.07

TABLE 28 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, MANITOBA
(continued)

Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
16	chernozemic	2 048	6-7		
	luvisolic	76 798	7		
	podzolic	122 162	7		
	brunisolc	7 884	6-7		
	gleysolic	2 662	5-6		
	organic	178 480	6		
	rockland	4 300	8		
				6-7	1 971.50
17	chernozemic	4 812	6-7		
	luvisolic	153	7		
				6-7	24.80
18	chernozemic	8 192	6-7		
	organic	102	6		
				6-7	41.40
19	chernozemic	2 046	6-7		
	luvisolic	102	7		
	regosolic	2 456	7		
	gleysolic	819	5-6		
	organic	13 413	6		
	rockland	4 915	8		
				6	2 375.00
20	chernozemic	614	6-7	6-7	3.07
Total					4 786.00

TABLE 29 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS,
SASKATCHEWAN

Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	chernozemic solonetzic	13 412 102	6-7 6	6-7	67.60
2	chernozemic solonetzic gleysolic	9 726 6 348 819	6-7 6 5-6	6	168.90
3	chernozemic regosolic gleysolic	19 041 102 102	6-7 7 5-6	6-7	96.30
4	chernozemic solonetzic	16 893 2 047	6-7 6	6-7	94.70
5	chernozemic	14 639	6-7	6-7	73.20
6	chernozemic gleysolic	16 380 102	6-7 5-6	6-7	82.40
7	chernozemic solonetzic regosolic gleysolic	14 640 716 1 945 409	6-7 6 7 5-6	6-7	88.60
8	chernozemic regosolic	16 736 1 023	6-7 7	6-7	88.80
9	chernozemic luvisolic	9 008 3 481	6-7 7	6-7	62.25
10	chernozemic luvisolic regosolic	10 648 2 252 819	6-7 7 7	6-7	68.60
11	chernozemic solonetzic regosolic	19 350 1 126 2 150	6-7 6 7	6-7	113.20

TABLE 29 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS,
SASKATCHEWAN (continued)

Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
12	chernozemic regosolic	12 592 1 228	6-7 7	6-7	69.20
13	chernozemic solonetzic regosolic	12 996 1 740 1 331	6-7 6 7	6-7	80.40
14	chernozemic luvisolic organic	10 649 15 663 6 553	6-7 7 6	6-7	164.40
15	chernozemic luvisolic regosolic	9 418 8 188 2 355	6-7 7 7	6-7	99.50
16	chernozemic luvisolic regosolic organic	8 293 11 467 614 102	6-7 7 7 6	7	20.50
17	chernozemic luvisolic	6 959 13 002	6-7 7	7	19.96
18	chernozemic luvisolic podzolic organic rockland	409 40 444 198 857 19 761 3 584	6-7 7 7 6 8	7	263.06
Total					1 721.70

TABLE 30 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, ALBERTA

Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	chernozemic solonetzic regosolic	18 227 2 662 409	6-7 6 7	6-7	106.50
2	chernozemic solonetzic	17 920 3 788	6-7 6	6-7	108.60
3	chernozemic rockland	13 414 307	6-7 8	6-7	68.60
4	chernozemic solonetzic regosolic	19 968 11 468 307	6-7 6 7	6	317.40
5	chernozemic solonetzic	15 564 512	6-7 6	6-7	80.40
6	chernozemic luvisolic	12 492 1 433	6-7 7	6-7	69.70
7	chernozemic solonetzic regosolic	13 619 6 246 102	6-7 6 7	6	199.67
8	chernozemic luvisolic	5 836 6 656	6-7 7	6-7	62.50
9	chernozemic luvisolic organic rockland	1 740 13 516 1 536 27 340	6-7 7 6 8	7	44.13
10	chernozemic solonetzic luvisolic	13 516 4 505 1 433	6-7 6 7	6-7	97.25

TABLE 30 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, ALBERTA
(continued)

Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
11	chernozemic	5 120	6-7	6-7	57.40
	solonetzic	102	6		
	luvisolic	5 939	7		
	organic	307	6		
12	chernozemic	1 638	6-7	6-7	636.00
	luvisolic	35 737	7		
	podzolic	9 113	7		
	brunisolc	3 891	6-7		
	regosolic	4 710	7		
	gleysolic	8 908	5-6		
	organic	53 862	6		
	rockland	9 318	8		
13	chernozemic	819	6-7	6-7	117.30
	solonetzic	1 024	6		
	luvisolic	17 408	7		
	gleysolic	1 536	5-6		
	organic	2 662	6		
14	luvisolic	21 401	7	7	31.70
	organic	5 222	6		
	rockland	5 120	8		
15	solonetzic	35 430	6	6-7	1 109.00
	luvisolic	94 412	7		
	podzolic	512	7		
	brunisolc	7 270	6-7		
	regosolic	7 372	7		
	gleysolic	17 920	5-6		
	organic	55 398	6		
	rockland	3 481	8		
Total					3 106.20

TABLE 31 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, BRITISH COLUMBIA

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
1	Alberni-Clayoquot	podzolic rockland	5 714 1 935	7 8	7	7.65
2	Bulkley - Nechako	luvisolic brunisollic rockland	55 171 7 663 8 428	7 6-7 8	7	71.26
3	Capital	podzolic brunisollic	1 100 1 191	7 6-7	6-7	11.46
4	Cariboo	chernozemic luvisolic podzolic brunisollic ice rockland	6 223 35 236 8 146 7 788 732 10 051	7 7 7 6-7 7 8	7	68.37
5	Central Fraser Valley	gleysolic	699	5-6	5-6	34.95
6	Central Kootenay	podzolic brunisollic gleysolic ice rockland	14 738 3 254 479 103 2 871	7 6-7 5-6 7 8	6-7	107.23
7	Central Okanagan	chernozemic luvisolic brunisollic	1 317 1 627 155	6 7 6-7	6-7	15.50
8	Columbia-Shuswap	podzolic luvisolic brunisollic gleysolic ice rockland	10 136 965 1 930 1 448 3 668 16 605	7 7 6-7 5-6 7 8	6-7	173.76

TABLE 31 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, BRITISH COLUMBIA (continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
9	Comox-Strathcona	podzolic	7 828	7	7-8	9.90
		ice	9 899			
		rockland	1 841	8		
10	Cowichan Valley	podzolic	1 970	7	7	3.34
		brunisollic	1 371	6-7		
11	Dewdney-Alouette	podzolic	1 464	7	6-7	15.59
		brunisollic	955	6-7		
		gleysolic	127	5-6		
		rockland	573	8		
12	East Kootenay	luvisolic	5 627	7	6-7	140.08
		podzolic	1 172	7		
		brunisollic	12 191	6-7		
		gleysolic	1 993	5-6		
		rockland	7 033	8		
13	Fraser-Cheam	luvisolic	353	7	6-7	53.35
		podzolic	4 938	7		
		brunisollic	4 497	6-7		
		gleysolic	176	5-6		
		rockland	705	8		
14	Fraser-Fort George	luvisolic	15 437	7	7-8	22.74
		podzolic	10 934	7		
		rockland	18 653	8		
		ice	459			
15	Greater Vancouver	podzolic	361	7	6-7	10.66
		burnisollic	1 771	6-7		
16	Kitimat-Stikine	luvisolic	524	7	7	94.69
		podzolic	45 458	7		
		brunisollic	12 255	6-7		
		rockland	31 003	8		
		ice	5 447			

TABLE 31 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, BRITISH COLUMBIA (continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
17	Kootenay Boundary	chernozemic luvisolic podzolic brunisollic	1 224 2 354 1 600 2 637	6-7 7 7 6-7	6-7	39.08
18	Mount Waddington	podzolic rockland ice	9 005 3 968 2 900	7 8	7-8	7.94
19	Nanaimo	podzolic brunisollic	924 1 093	7 6-7	6-7	10.09
20	North Okanagan	chernozemic luvisolic podzolic	837 1 673 5 229	6-7 7 7	7	7.74
21	Ocean Falls	podzolic luvisolic brunisollic rockland ice	10 095 1 009 1 211 9 893 2 624	7 7 6-7 8	7	24.83
22	Okanagan - Similkameen	chernozemic luvisolic brunisollic	3 209 4 011 3 309	6-7 7 6-7	6-7	52.65
23	Peace River - Liard	solonetzic luvisolic brunisollic regosolic organic rockland	1 335 75 496 20 646 1 643 38 005 55 672	6 7 6-7 7 6 8	6-7	963.99
24	Powell River	podzolic rockland ice	2 219 1 513 1 311	7 8	7-8	2.52
25	Skeena A	podzolic	15 954	7	7	15.95

TABLE 31 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, BRITISH COLUMBIA (continued)

No.	Census Division	Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
26	Squamish-Lillooet	chernozemic	714	6-7	7	16.32
		luvisolic	1 020	7		
		podzolic	7 548	7		
		brunisollic	2 754	6-7		
		rockland	2 652	8		
		ice	1 428			
27	Stikine	luvisolic	10 138	7	6-7	559.39
		brunisollic	37 583	6-7		
		rockland	55 676	8		
		ice	8 478			
28	Sunshine Coast	podzolic	2 321	7	6	38.35
		gleysolic	606	5-6		
		rockland	908	8		
29	Thompson-Nicola	chernozemic	13 057	6-7	6-7	372.07
		luvisolic	44 373	7		
		podzolic	9 129	7		
		brunisollic	3 609	6-7		
		rockland	3 715	8		
		ice	530			
Total						2 951.50

TABLE 32 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, NORTHWEST TERRITORIES

		Area		Division	Sulphur
District	Soil Type	(km ²)	Rank	Rank	Emissions (10 ⁷ g/yr)
MacKenzie	luvisolic	102	7	6-7	1 380.00
	podzolic	15 360	7		
	brunisollic	87 756	6-7		
	regosolic	105 881	7		
	gleysolic	17 817	5-6		
	organic	44 339	6		
	rockland	5 324	8		
Keewatin	podzolic	1 228	7	6-7	615.00
	brunisollic	97 792	6-7		
	regosolic	23 347	7		
	rockland	1 331	8		
Franklin	regosolic	248 729	7	7	282.10
	rockland	33 382	8		
Total					2 277.10

TABLE 33 CENSUS DIVISION RANKING AND SULPHUR EMISSIONS, YUKON

Soil Type	Area (km ²)	Rank	Division Rank	Sulphur Emissions (10 ⁷ g/yr)
brunisollic	66 764	6-7	6-7	495.00
regosolic	10 444	7		
gleysolic	3 584	5-6		
rockland	18 227	8		
Total				495.00

5.1.2 Vegetation. The estimate of sulphur emissions from vegetation, summarized in Table 34, was obtained by applying the sulphur productivity rankings derived from the consideration of soil climates (section 4.2.2). In an alternate, more detailed approach, a determination of sulphur emissions by typical vegetation occupying various soil temperatures is given in Table 35. The two estimates are similar, the first being 8 594 tonnes and the second, 8 907 tonnes.

TABLE 34 ESTIMATED SULPHUR EMISSIONS FROM VEGETATION

Vegetation	Area (10 ⁶ km ²)	Rank	Sulphur Emissions (t as S)
Tundra continuous permafrost	2.76	10	28
Tundra widespread permafrost	2.36	9	236
Open-shrub forest	2.95	8	2 950
Coniferous and mixed forests	0.949	7-8	4 750
Deciduous forest	0.126	7-8	630
Total			8 594

TABLE 35 ESTIMATED SULPHUR EMISSIONS FROM VEGETATION IN VARIOUS SOIL TEMPERATURE CLIMATES

	Arctic and Sub-Arctic	Cryoboreal	Boreal	Mesic	Total
Rank	9-10	8-9	7-8	8	
S Productivity (g S/m ² /yr)	5×10^{-5}	5×10^{-4}	5×10^{-3}	10^{-3}	
Province	Emissions (10 ⁶ g S/yr)				
Newfoundland and Labrador	5.6	132	--	--	137.6
Prince Edward Island	--	--	200	--	200.0
Nova Scotia	--	2	220	4	226.0
New Brunswick	--	7.5	270	--	277.5
Quebec	19.7	337.5	1 410	5	1 772.2
Ontario	3.3	134	2 505	56	2 698.3
Manitoba	8.3	154	390	--	552.3
Saskatchewan	1.9	158	1 085	--	1 244.9
Alberta	2.9	213.5	800	--	1 016.4
British Columbia	14.8	262.5	505	--	782.3
Canada Total	56.5	1 401.0	7 385	65	8 907.5

5.1.3 Aquatic. The marine divisions presented in Table 36 are composed of the various marine classifications that were ranked for sulphur productivity in section 4.2.3 (Table 17). An average sulphur rank was derived for each division from the data of Owens (1977), which provided the relative frequency of each classification in the division. The emission rate corresponding to the sulphur rank was then multiplied by the area and the ice-free period to obtain the estimates for coastal emissions of sulphur (Table 37).

The estimated biogenic sulphur production from Canadian lakes is presented in Table 38.

TABLE 36 SULPHUR EMISSION RANKING FOR COASTAL SHORELINE HABITATS

Coast	Marine Division	Area (km ²)	Sulphur Rank	Ice-Free Period	Classification (See Table 17)
Pacific (Figure 12)	1	1 044	4	1.0	III 11, IV 12
	2	10 962	8	1.0	I4, II 5
	3	1 740	8	1.0	I2, II 5
	4	72 732	10	1.0	I3
	5	55 854	10	1.0	I2,
	6	10 614	8	1.0	I4, II 6
Arctic (Figure 13)	1	29 200	6 (8)*	0.3	II 5, III 10
	2a	36 400	6 (7)	0.2	III 10
	2b	42 700	8 (9)	0.2	I2, II 5
	3	42 000	10 (-)	0.2	I2, I3
	4	12 400	10 (-)	0.2	I3
	5	10 000	10 (-)	0.1	II, II 5
	6	3 600	10 (-)	0.0	II, II 5
	7	34 400	10 (-)	0.1	II, II 5
	8	11 600	9 (-)	0.1	II, II 5
	9	60 000	9 (-)	0.2	I2, II 5
	10	7 200	9 (-)	0.2	II, II 5, II 6
	11	4 400	5 (7)	0.2	II 6, IV 12
	12	3 200	8 (10)	0.2	I4, II 6
Atlantic (Figures 8, 9)	1	45 018	10	0.8	II, II 7
	2	21 033	10	0.4	II, II 7
	3	3 690	4	0.6	III 11, III 10
	4	22 509	5	0.6	II 6, II 7
	5	11 439	8	0.9	I2, II 7
	6	3 321	6	0.9	I4, III 10
	7	738	5	1.0	II 6
Great Lakes (Figure 10)	1	21 964	7	0.6	II 5
	2	4 913	5	0.6	II 6
	3	2 312	7	0.6	II 5
	4	8 381	7	0.6	II 5
	5	12 427	7	0.6	II 5
	6	4 913	6	0.6	II 5, II 7
	7	1 445	5	0.6	II 6
	8	14 739	10	0.6	I2
	9	32 946	10	0.6	II, I2

* Rank adjusted for climatic differences; "-" indicates no sulphur production.

TABLE 37 COASTAL SULPHUR EMISSIONS IN CANADA

Coast	Marine Division	Emissions (10 ⁶ g S/yr)
Pacific (Figure 12)	1	10 440
	2	11
	3	2
	4	1
	5	1
	6	11
Total		10 466
Arctic (Figure 13)	1	9
	2a	73
	2b	1
	11	9
	12	< 1
Total		92
Atlantic (Figures 8, 9)	1	< 1
	2	< 1
	3	22 140
	4	13 505
	5	10
	6	299
	7	738
Total		36 692
Great Lakes (Figure 10)	1	132
	2	2 948
	3	14
	4	50
	5	75
	6	295
	7	867
	8	< 1
	9	< 1
Total		4 381
Canada Total		51 631

TABLE 38 ESTIMATED BIOGENIC SULPHUR EMISSIONS FROM FRESHWATER LAKES IN CANADA

Province	Total Lake Area (10^9 m^2)	Lake Type	Lake Area (10^9 m^2)	Rank	Sulphur Emissions (10^6 g S/yr)	Total Sulphur Emissions by Province (10^6 g S/yr)
Newfoundland	34.0	Eutrophic	4	6-7	200	
		Other	30	9	3	203
Nova Scotia	2.6	Eutrophic	1.0	6	100	
		Other	1.6	8	2	102
New Brunswick	1.3	Eutrophic	0.3	6	30	
		Other	1.0	8	1	31
Quebec	184.0	Eutrophic	13	6	1 300	
		Other	171	8	171	1 471
Ontario	177.0	Eutrophic	34	6	3 400	
		Other	143	8	143	3 543
Manitoba	102.0	Eutrophic	52	6-7	2 600	
		Other	50	8	50	2 650
Saskatchewan	82.0	Eutrophic	48	6-7	2 400	
		Other	34	8	34	2 434
Alberta	17.0	Eutrophic	13	6-7	650	
		Other	4	8	4	654
British Columbia	18.0	Eutrophic	8	6	800	
		Other	10	8	10	810
Canada Total						11 898

Note: No estimate was made for freshwater lakes of the Territories and the Yukon. Emissions from the few lakes in Prince Edward Island are insignificant.

5.2 Other Natural Emissions

This section presents the estimates of sulphur emissions from sea spray and lake spray (Table 39). The estimated sea-salt-sulphate emissions are from the 320-km fishing zone on the Pacific and Atlantic coasts, the entire area of Hudson Bay, and the area of the Beaufort Sea south of the permanent ice pack. The annual sea and lake sulphate emissions were estimated from rates derived in section 4.3.1. The estimated lake sulphate emissions amounted to only 7 tonnes for those lakes having an area greater than 1 000 km². The annual emissions from forest fires have been presented previously in Table 19.

TABLE 39 ANNUAL SULPHUR EMISSIONS FROM SEA-SALT SPRAY IN CANADA

Region	Area (km ²)	Flux (10 ⁶ g S/km ² /yr)	Emissions (10 ⁶ g S/yr)
Pacific Ocean	390 000*	0.07	27 300
Atlantic Ocean	520 000*	0.17	88 400
Labrador Sea	320 000*	0.04	12 800
Hudson Bay	820 000	0.07	57 400
Beaufort Sea	50 000	0.06	3 000
Total			188 900

* Area of coastal waters to 320-km limit

6 DATA GAPS AND UNCERTAINTIES

The investigation of natural emissions of sulphur has only recently gained momentum. As a consequence, only preliminary data, if any, are available as an aid in quantifying emission rates of natural compounds. In addition, the validity of the current measurement techniques is being re-evaluated.

Global sulphur budgets, with their inherent weakness of using backfitting estimates to balance the sulphur cycle, do not provide accurate data for determining natural emissions on a regional basis. These budgets also cannot account for regional differences in sulphur production, which vary with factors such as soil climate, growing season, ice cover, and prevalence of water bodies. Similarly, applying spot measurements of fluxes (which in themselves may not be accurate) to large scale integrated features of soils and hydrology leads to significant inaccuracies.

The estimates in this report, out of necessity, were generated using the spot-measurement approach, modified by a semi-quantitative interpretation of the more productive generation mechanisms.

The biogenic natural sulphur emissions estimated for Canada are about 0.3 Tg S/yr compared with a value of about 5 Tg S/yr reported by Katz (1977). Katz's value was derived by proportioning the estimated budget of the Northern Hemisphere (by Kellogg et al. 1972) with the ratio of Canadian land area to hemispheric land area.

This approach does not take into account the extreme variability of climatic, terrestrial, and hydrographic conditions in the hemisphere. Most evidence indicates a higher production of sulphur by biogenic sources in equatorial areas. Biogenic fluxes have been shown to increase by two orders of magnitude as the temperature increases from 5-10°C to 30°C (Adams 1978a, Georgii 1978). The latter temperature is typical of equatorial regions while the former is typical of a large part of Canada. If this temperature factor is considered, it appears that Katz's (1977) estimate is too high, possibly by an order of magnitude.

The approach in this study has been to use average soil and marine conditions on a scale of about 200 km² and a logarithmic ranking of sulphur productivity. Contributions by high-production areas of smaller size may consequently be underestimated. The range of variation in the present estimate of 0.3 Tg S/yr could be within plus or minus one order of magnitude (i.e., 0.03 - 3). However, the limitations of the Katz (1977) approach

and the possible underestimations in this study suggest that biogenic sulphur emissions in Canada range from 0.3 to 1.0 Tg S/yr.

The validity of current measurement and analytical techniques must be ascertained before a more accurate estimate of biogenic sulphur emissions is made. A U.S. National Science Foundation workshop on the chemistry of the troposphere, held in the fall of 1978, concluded that none of the techniques now used to estimate biogenic sulphur emissions are reliable (Hitchcock personal communication).

The chamber method used by various researchers in the field appears to inhibit H_2S emissions much more than emissions of organic sulphur compounds. In addition, this technique may also disturb sediment-air and soil-air interfaces. Biogenic H_2S escapes to the air only when the anaerobic producing medium is close to the atmospheric boundary layer. If an overlying aerobic layer is disturbed by an *in situ* measurement device, erroneously high concentrations of biogenic sulphides may be detected in the air above the interface.

Vertical mean profiles of natural sulphur concentration data are commonly used to calculate the flux of a sulphur compound into the atmosphere. This gradient technique assumes that the horizontal extent of the emitting source is large compared with the measuring altitude and that there are no temporal variations in the emission rate. This is rarely or never achieved; H_2S production has been shown to be extremely variable in both space and time.

The relative contributions of gaseous compounds other than H_2S to total sulphur fluxes for biogenic sources has only been examined by Adams (1978a). This is a serious data gap since there is no comparison available to obtain an indication of flux variability. Consequently, the emissions from biogenic sources estimated from soils and marine areas are only representative of the evolution of H_2S .

The information available indicates that the volatile organic sulphur compounds are released by different soil types at relatively similar rates. Such emissions appear to be a general feature of soils. It appears, at this time, that sulphur emission variability is attributable mainly to H_2S . Emission of other compounds from various soil types is more uniform. While H_2S may be produced in apparently aerobic soils, much more is produced in waterlogged and reducing soils.

The behaviour of methylating and related bacteria involved in the production of DMS, CH_3SH and related compounds is poorly understood, so that the relationship

between soil sulphur production and soil conditions in other than anaerobic soils is unknown.

Release rates of DMS (Lovelock et al. 1972) from vegetation were used in this study in estimating sulphur emissions from vegetation. Other organic sulphur compounds, potentially produced by plants, were not accounted for because of lack of information. Also, there are no data on the mechanism for production of volatile sulphur compounds from living and senescent plants, although production during enzymic breakdown of protein material is possible.

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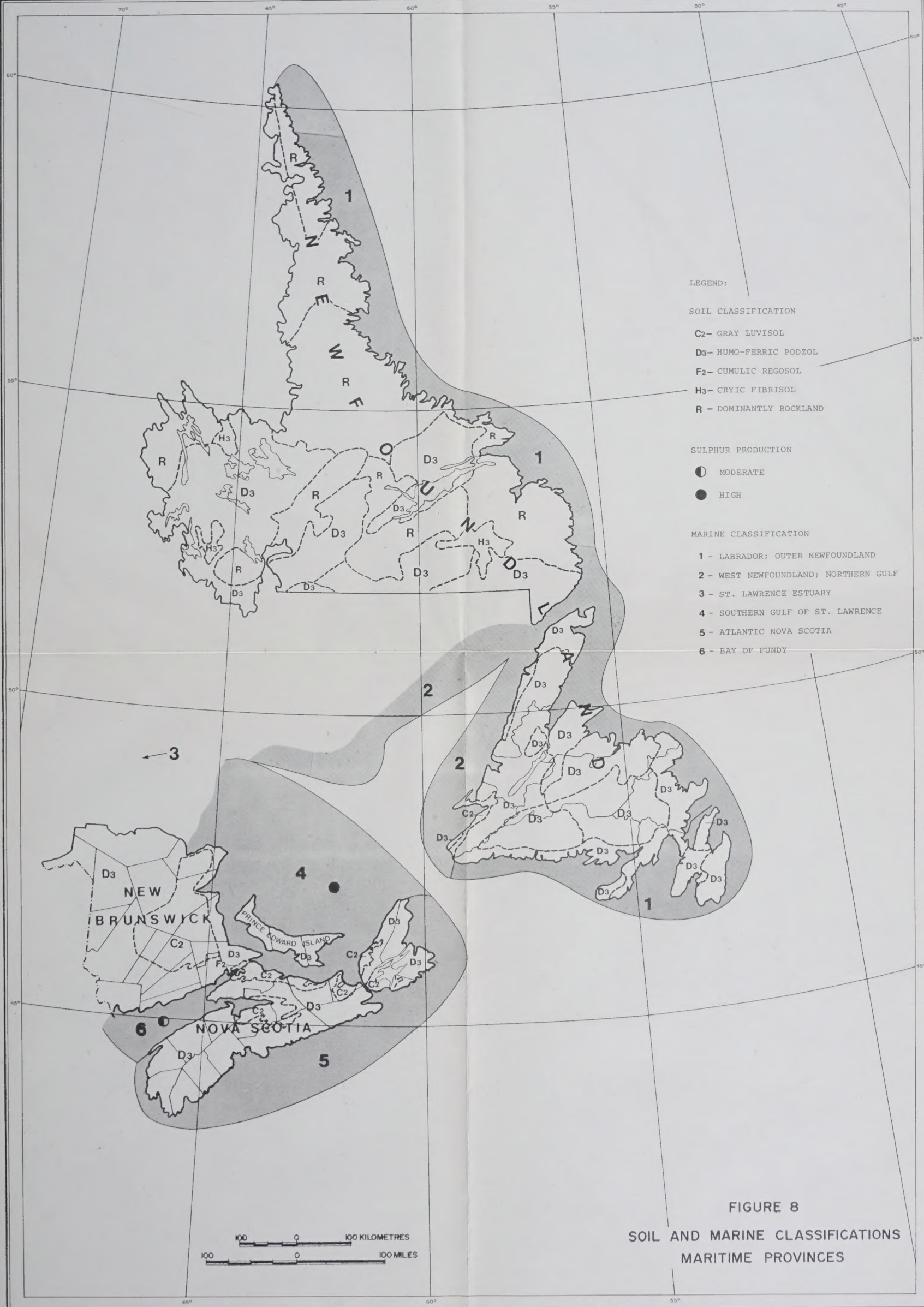
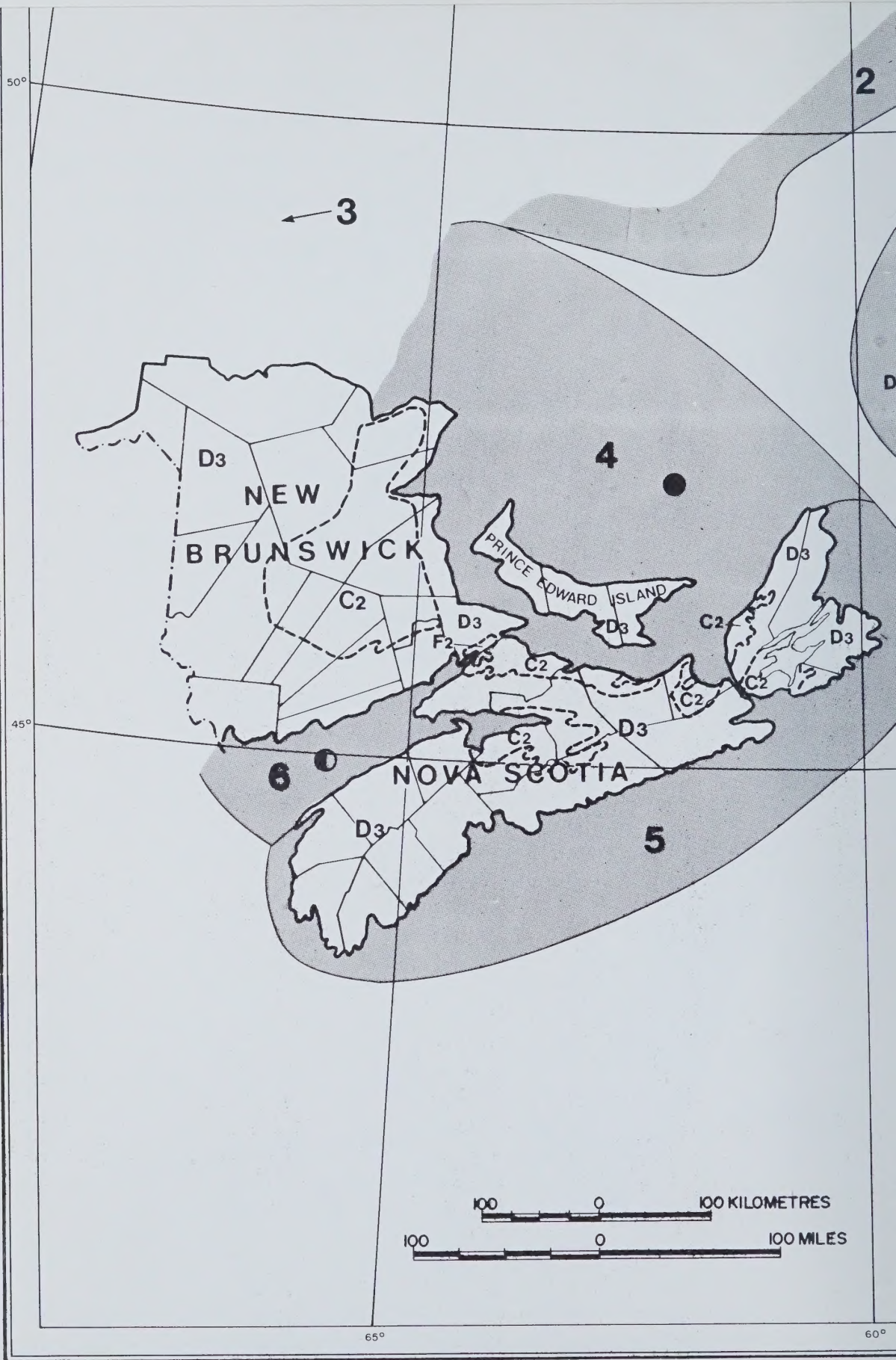


FIGURE 8

SOIL AND MARINE CLASSIFICATIONS

MARITIME PROVINCES



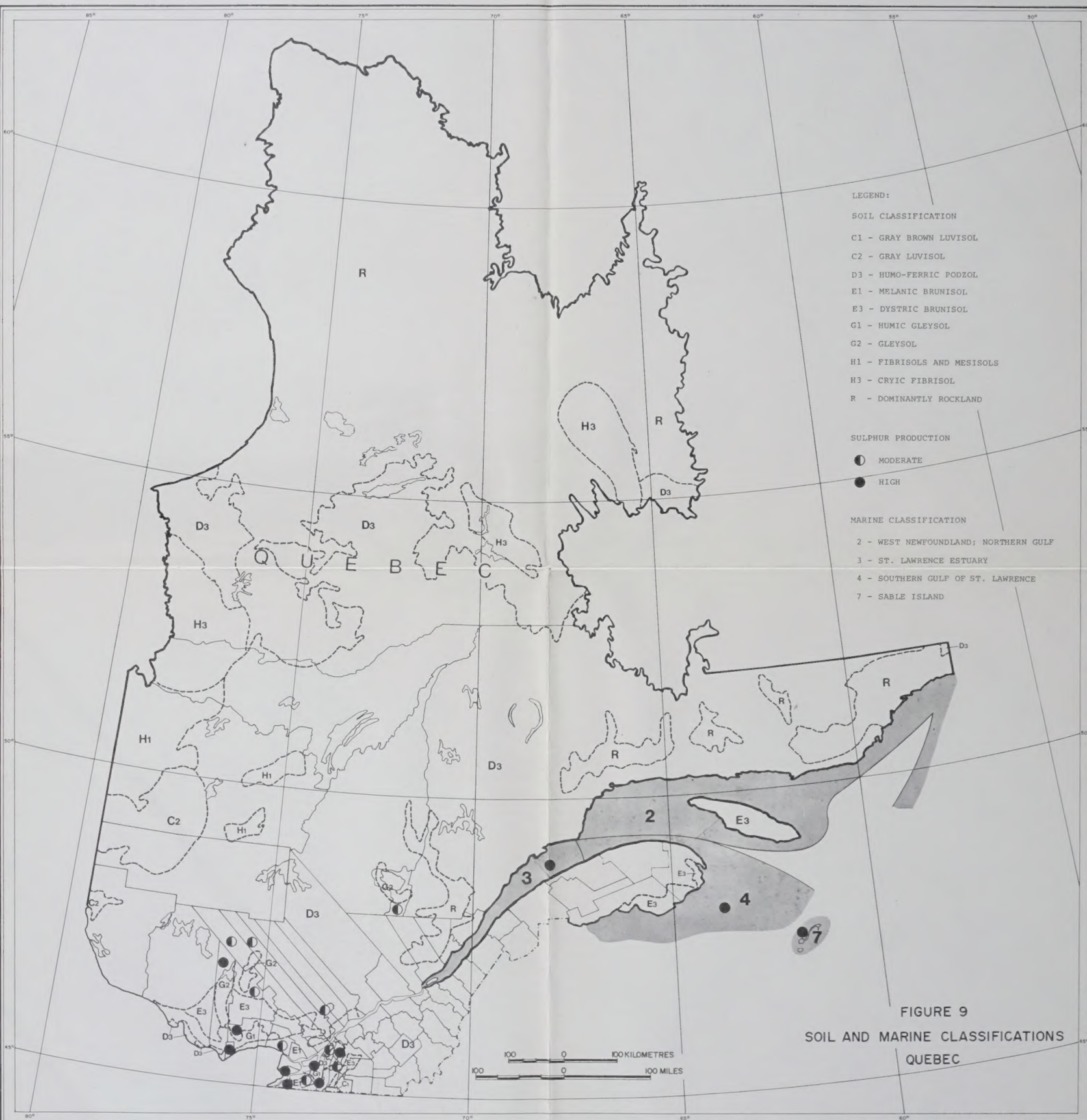
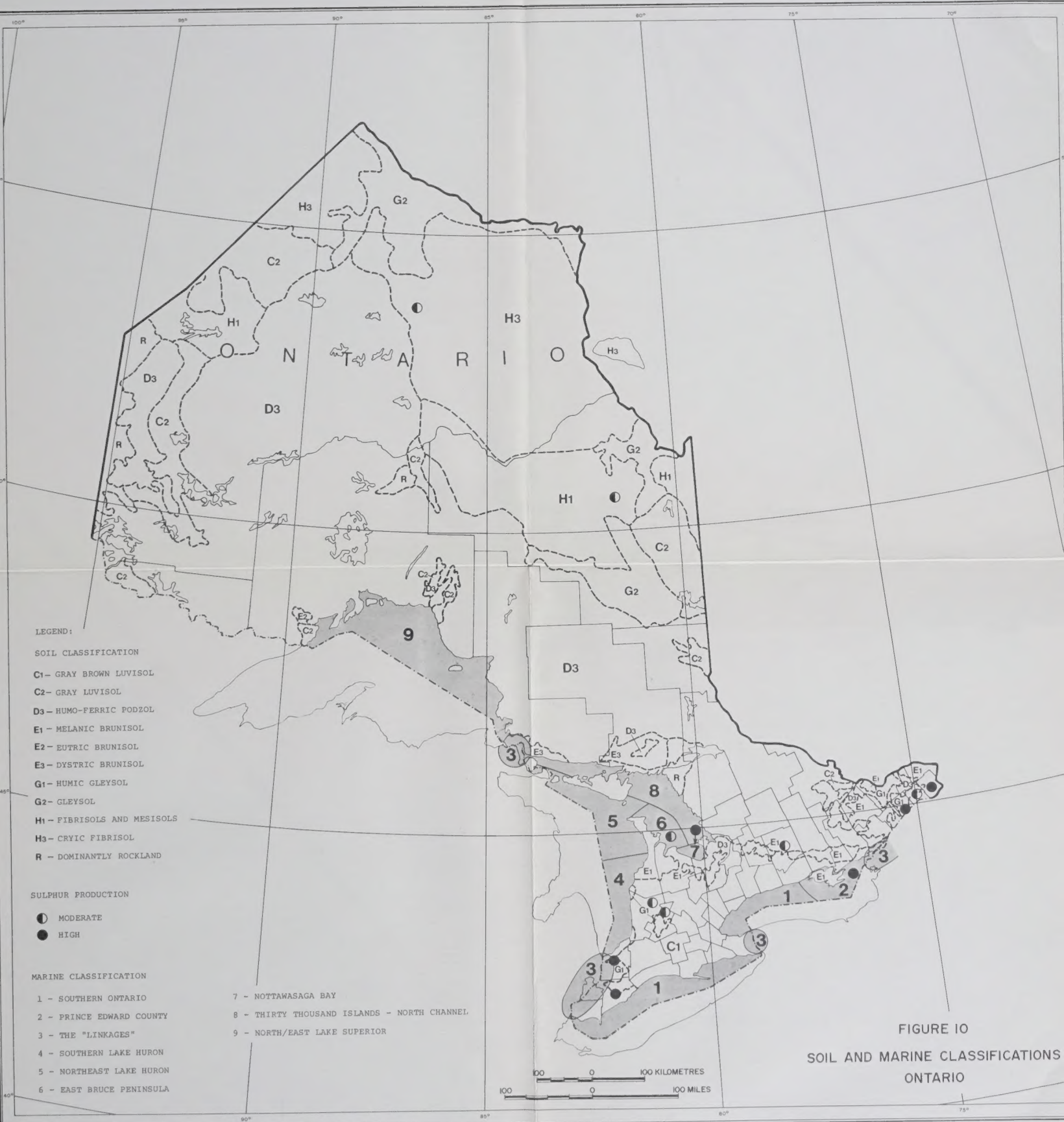


FIGURE 9
SOIL AND MARINE CLASSIFICATIONS
QUEBEC





LEGEND:

SOIL CLASSIFICATION

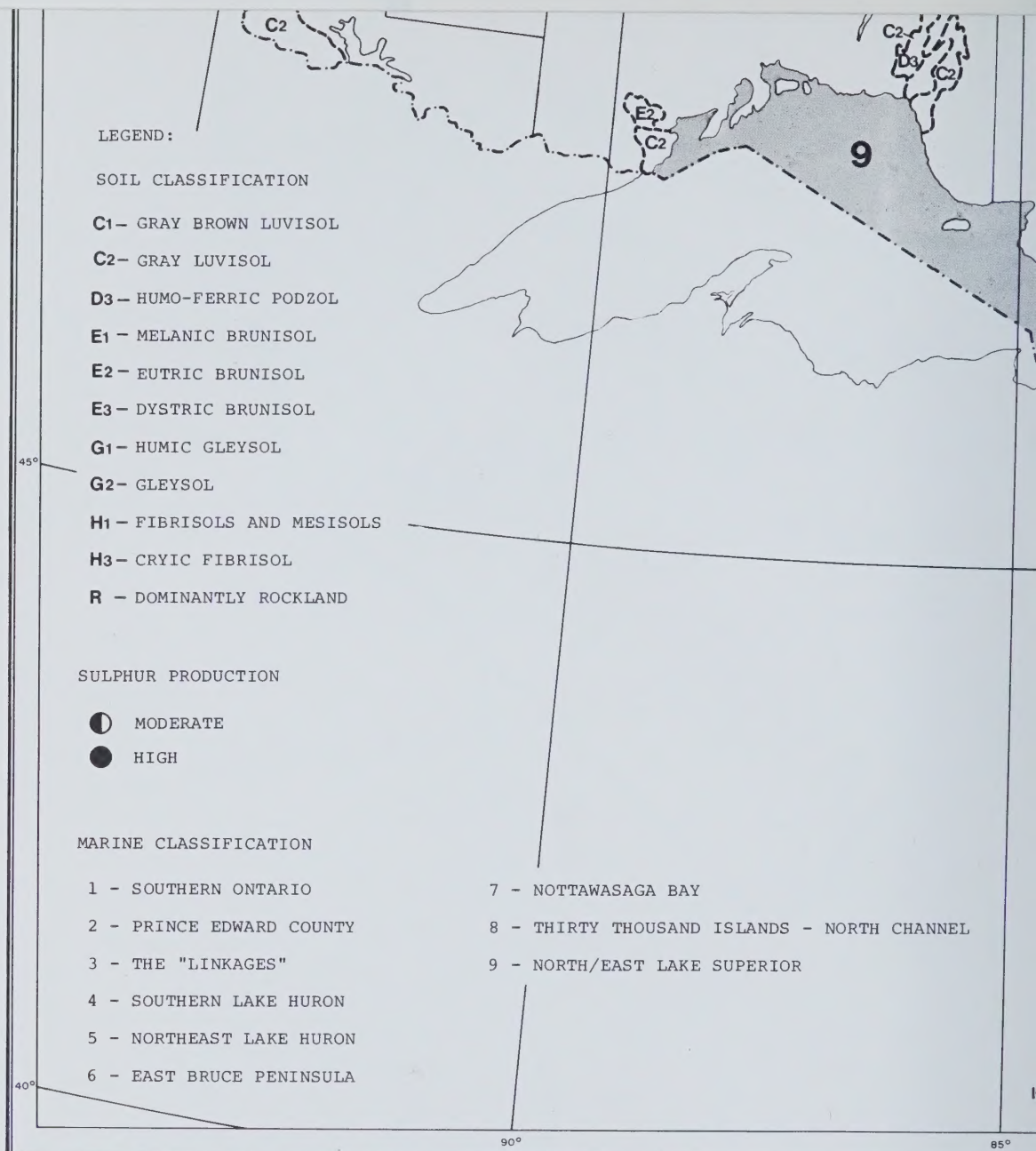
- C1- GRAY BROWN LUVISOL
- C2- GRAY LUVISOL
- D3- HUMO-FERRIC PODZOL
- E1 - MELANIC BRUNISOL
- E2- EUTRIC BRUNISOL
- E3- DYSTRIC BRUNISOL
- G1- HUMIC GLEYSOL
- G2- GLEYSOL
- H1 - FIBRISOLS AND MESISOLS
- H3- CRYIC FIBRISOL
- R - DOMINANTLY ROCKLAND

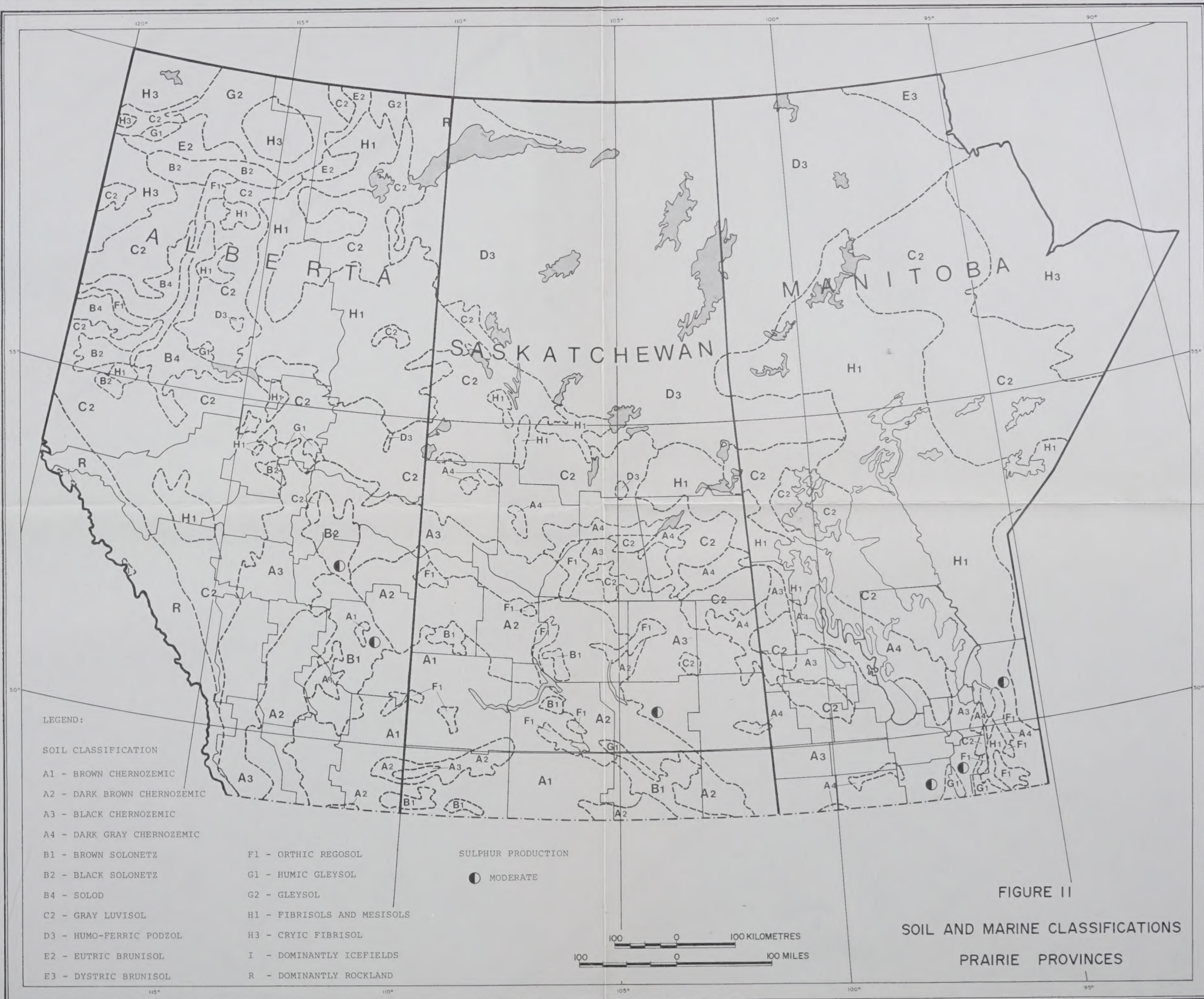
SULPHUR PRODUCTION

- ◐ MODERATE
- HIGH

MARINE CLASSIFICATION

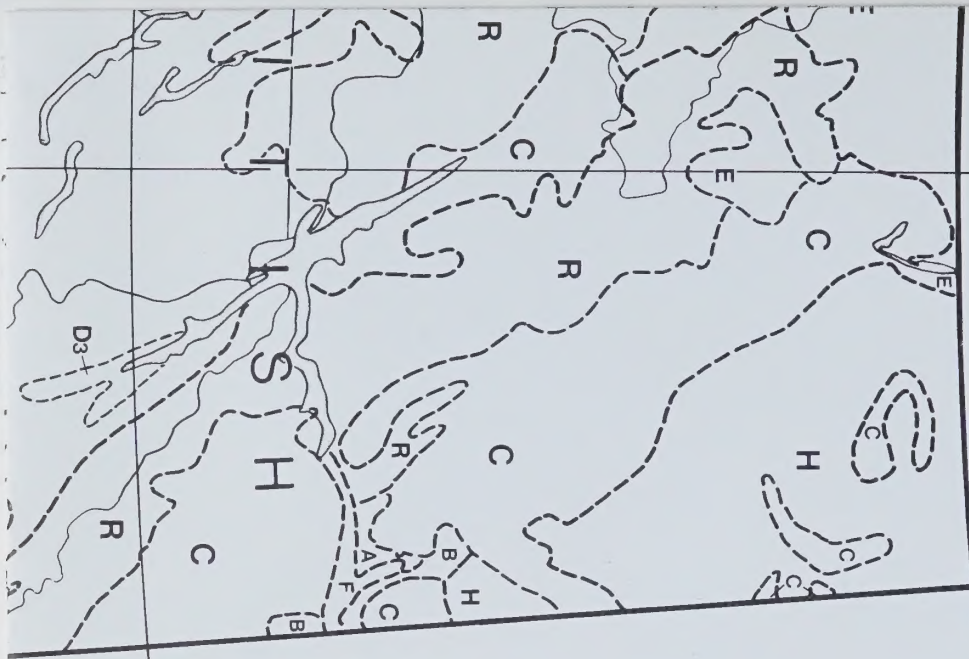
- | | |
|--------------------------|---|
| 1 - SOUTHERN ONTARIO | 7 - NOTTAWASAGA BAY |
| 2 - PRINCE EDWARD COUNTY | 8 - THIRTY THOUSAND ISLANDS - NORTH CHANNEL |
| 3 - THE "LINKAGES" | 9 - NORTH/EAST LAKE SUPERIOR |
| 4 - SOUTHERN LAKE HURON | |
| 5 - NORTHEAST LAKE HURON | |
| 6 - EAST BRUCE PENINSULA | |





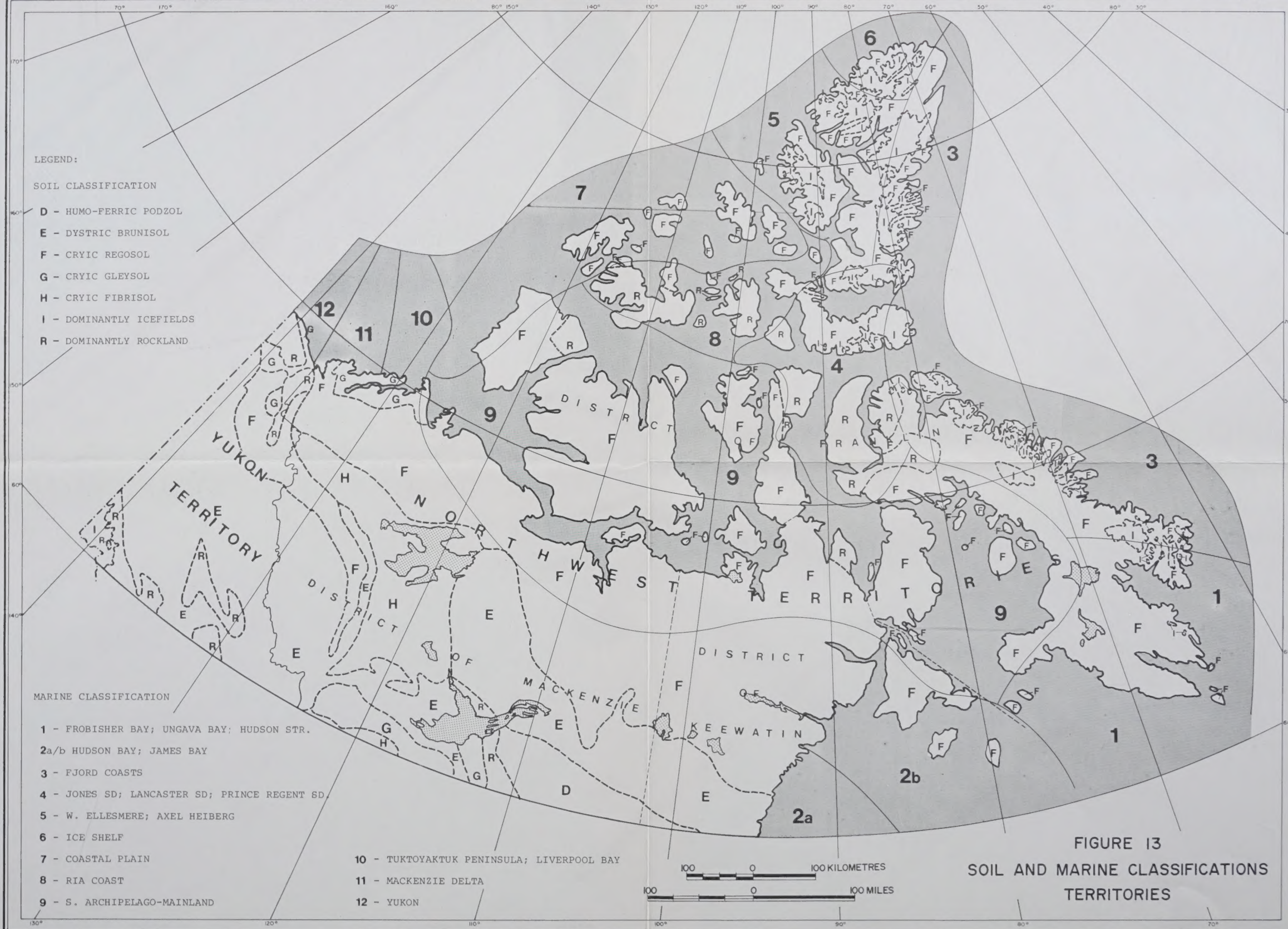






55°

60°



LEGEND:

SOIL CLASSIFICATION

- D - HUMO-FERRIC PODZOL
- E - DYSTRIC BRUNISOL
- F - CRYIC REGOSOL
- G - CRYIC GLEYSOL
- H - CRYIC FIBRISOL
- I - DOMINANTLY ICEFIELDS
- R - DOMINANTLY ROCKLAND

MARINE CLASSIFICATION

- 1 - FROBISHER BAY; UNGAVA BAY; HUDSON STR.
- 2a/b HUDSON BAY; JAMES BAY
- 3 - FJORD COASTS
- 4 - JONES SD; LANCASTER SD; PRINCE REGENT SD
- 5 - W. ELLESMERE; AXEL HEIBERG
- 6 - ICE SHELF
- 7 - COASTAL PLAIN
- 8 - RIA COAST
- 9 - S. ARCHIPELAGO-MAINLAND
- 10 - TUKTOYAKTUK PENINSULA; LIVERPOOL BAY
- 11 - MACKENZIE DELTA
- 12 - YUKON

FIGURE 13
SOIL AND MARINE CLASSIFICATIONS
TERRITORIES

